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FLUORIDE STUDIES RELATED TO THE HUMAN DIET[1]

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Abstract

Analyses of whole meals and beverages indicated that the amount of fluoride normally present in the adult diet is quite low but the ingestion of tea or high fluoride waters greatly increases it. The fluoride content of cow's milk from low and high water-fluoride areas was determined. Analyses of some baby foods showed that the fluoride content of certain cereals containing bonemeal is high. The influence on the infant diet of these cereals and of water and milk is illustrated.

Introduction

The discovery of the role of fluorine (6) in the prevention of dental caries has initiated considerable research on this element and its biological effects. Fluorides are not only beneficial in decreasing dental caries incidence, but they are also potentially toxic in nature and the causative factor in the condition known as "mottled enamel" (3, 19).

Drinking water is the most important source of fluorides, and the content may vary from negligible amounts to 14 p.p.m. One part per million fluoride in the communal water supply is considered optimum for the prevention of dental caries with a minimum occurrence of "mottled enamel" (7). To test the value of added fluoride through long-range experiments, the drinking water of Brantford, Ont., and of a number of communities in the United States has been artificially fluorinated to this optimum degree.

The occurrence of fluorides in food is wide and variable although, with the exception of tea and fish, the amount is usually quite small. However, the amount naturally present in foods and its influence on total fluoride ingestion are important and have to some extent been neglected. The studies reported here were undertaken in an effort to obtain information concerning the fluoride content of the diet in southern Ontario and some of the factors that influence it.

Experimental

To learn the amount of fluoride in a normal mixed diet, it was decided to make analyses on whole meals and beverages of various types. The

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meals were obtained from a local restaurant and were prepared for sampling by mixing in a Waring blender.

It also seemed of interest to determine whether the foods produced in low water-fluoride districts contain less fluoride than those produced in high water-fluoride areas and thus affect the total fluoride ingestion. Milk was chosen for analysis in the study of this relationship. It is consumed by a large percentage of the population, especially those most affected by fluorides, the children, and it is comparatively easy to obtain representative samples of homogenized milk. Furthermore, there is lack of agreement concerning the influence of fluorides present in the cows' drinking water on the fluoride content of the milk produced. To investigate this question, the cities of Kitchener and Stratford were chosen as suitable centers from which milk and water samples could be obtained. Figures from the Ontario Department of Health indicated that Kitchener has negligible fluoride in its water supply while Stratford has approximately optimum fluoride. The fluoride content of the communal water supply of each of these two cities was determined for three consecutive months. Homogenized milk from three dairies in each of these cities was analyzed for fluoride for three consecutive weeks.

In addition to milk, a number of common baby foods are included in the diet of infants and young children. Because of the importance of fluoride ingestion by children, some of these foods were assayed for their fluoride content. They were procured from the usual retail sources.

Method of Analysis

The reagents and method used were essentially those outlined for the determination of fluorine in food and water in the *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists* (*2*) with a few modifications.

The method involves drying and ashing of the material with a fluoride fixative if organic matter is present, distillation from perchloric acid, and a back-titration with thorium nitrate and potassium fluosilicate.*

Calcium hydroxide solution was used as a fluoride fixative in the milk analyses. The samples were dried and then ashed in a muffle furnace at 580° C. for three hours. In all other analyses requiring a fixative, the calcium hydroxide solution was replaced by magnesium acetate solution (5).

A special distillation apparatus with ground glass joints and a distilling head was obtained from the Scientific Glass Apparatus Co., Bloomfield, N.J. A solution containing concentrated sulphuric acid diluted with water 1 : 1 was boiled down to fumes each day in the still, and between each determination the still was washed with hot 10% sodium hydroxide. The prepared sample was distilled at 135° C. ± 2°. Collection was started at 110° C., since it was learned through recovery experiments that some of the hydrofluosilic acid came over before 135° C.

* *Obtained from P. A. Clifford, Food and Drug Administration, Washington, D.C.*

Potassium fluosilicate was used in the back-titration rather than sodium fluoride since it appears that dilute silico-fluoride solutions such as occur in the distillate do not titrate like the simple fluorides (4).

Results and Discussion

Meals and Beverages

From this one series of analyses of Toronto meals reported in Table I, food-borne fluoride appears to amount to 0.18–0.30 mgm. per day. It

TABLE I

FLUORIDE CONTENT OF MEALS

Meals	Fluoride content	
	P.p.m. dry wt.	Total fluoride, mgm.
1. Breakfast (juice, cream of wheat, toast, marmalade)	1.04, 0.77	0.15
2. Lunch (fruit salad, rolls and butter, dessert)	0 0	0
3. Dinner *A* (tomato juice, halibut, potatoes, spinach, bread and butter, dessert)	1.04, 0.92	0.15
4. Dinner *B* (tomato juice, beef, potatoes, macedoine vegetables, bread and butter, dessert)	0.11, 0.26	0.03

should be noted that the servings of these restaurant meals were rather small. As was anticipated, dinner *A* had a high fluoride content because of the fish and spinach, which are generally comparatively high in fluoride. In the case of the breakfast, the high result was unexpected, but might be accounted for by the cream of wheat. McClure (14) suggests that 0.25–0.55 mgm. food-borne fluoride are ingested daily, with emphasis on the lower end of the range. Armstrong and Knowlton (1) found a fluoride content of 0.27–0.32 mgm. in the average daily food.

Figures in Table II indicate that a tea infusion provides approximately 1 p.p.m. fluoride, which is the optimum content for water. Cheap tea appears to contain more fluoride than expensive tea, which Reid (17) suggests is due

TABLE II

FLUORIDE CONTENT OF BEVERAGES

Beverages	Fluoride content	
Cheap tea infusion	117.0,	126.6 μgm./100 ml.
Expensive tea infusion	105.3,	91.6 μgm./100 ml.
Coffee infusion	0.88,	μgm./100 ml.
Coca cola	0.06,	0.07 p.p.m.
Toronto water	0.12,	0.11 p.p.m.
Toronto milk (homogenized)	0.06,	p.p.m.

to the fact that older leaves are used in cheaper teas and fluoride tends to accumulate with age. More analyses are needed to confirm this theory.

A meal containing 0.15 mgm. fluoride plus an eight ounce glass of milk has a fluoride content of approximately 0.17 mgm. fluoride. The same meal, substituting one cup of tea for the milk, would have a fluoride content of approximately 0.35 mgm. fluoride. Thus the ingestion of tea greatly increases the fluoride content of the diet.

Water-Milk Survey

The figures in Table III indicate that Stratford water has a fluoride content that is considered approximately optimum, while Kitchener water has a low

TABLE III

FLUORIDE CONTENT OF WATER FROM KITCHENER AND STRATFORD MUNICIPAL SUPPLIES FOR THREE CONSECUTIVE MONTHS

Month	Fluoride content, p.p.m.	
	Kitchener	Stratford
February	0.16, 0.13	1.25, 1.27
March	0.19, 0.16	1.31, 1.28
April	0.17, 0.17	1.29, 1.33

fluoride content. The results appeared consistent over the three months studied and confirmed the choice of these cities for investigation.

From the results in Table IV it may be seen that the fluoride content of milk is quite low. McClure (14) gives the normal range as 0.1–.02 p.p.m. fluoride. It was impossible to ascertain the source of the water ingested by the cows and because of the difficulty in securing samples, the milk from the two areas was not obtained at the same time.

TABLE IV

FLUORIDE CONTENT OF MILK FROM KITCHENER AND STRATFORD FOR THREE CONSECUTIVE WEEKS

City	Dairy	Fluoride content, p.p.m.		
		1st week	2nd week	3rd week
Kitchener (April)	#1	0.03, 0.04	0.13	0.11
	#2	0.03	0.08	0.09
	#3	0.06	0.12	0.09
Stratford (February)	#4	0.09	0.16	0.17
	#5	0.14	0.13	0.17
	#6	0.11	0.11	0.16

Although the results for these samples when analyzed statistically show a significant difference between the fluoride content of milk from Kitchener and from Stratford, it is appreciated that the range within which fluoride occurs in the milk is quite low and this difference may be only apparent. McClendon and coworkers (13) found an inverse ratio between the fluoride content of the milk supply and the incidence of dental caries. Smith, Smith, and Vavich (20) found that even when cows were given sodium fluoride in high concentration in their drinking water (up to 500 p.p.m.) the fluoride was not transmitted in large quantities to the milk, but was largely excreted by the kidneys. However, the fluoride content of the milk rose from 0.0–0.3 p.p.m. when the fluoride content of the drinking water rose from 0.02–3.0 p.p.m. Hart and Elvehjem (9) and Phillips, Hart, and Bohstedt (16) state that the fluoride content of milk is unaffected by the ingestion of fluorides, and this conclusion is upheld by McClure in a recent summary (14).

Baby Foods

In Table V the high fluoride content of Pablum and Pabena is particularly interesting. The greater part of this is assumed to come from bonemeal,

TABLE V

FLUORIDE CONTENT OF BABY FOODS

Baby foods	Fluoride content			
Heinz strained spinach	6.8,	8.2		p.p.m. dry wt.
Heinz " carrots	0			
Heinz " beans	0.06,	0.10		p.p.m. dry wt.
Pablum	13.7	12.2,	12.6	p.p.m.
Pabena	11.3	12.1		p.p.m.

which constitutes 2% of the Pablum. It might be noted here that some bonemeal capsules analyzed were found to have a fluoride content of 246 and 285 p.p.m.

Table VI shows the influence of the fluoride content of water, milk, and Pablum on the fluoride ingestion of infants in Kitchener and Stratford.

TABLE VI

DAILY FLUORIDE CONTENT OF WATER, MILK, AND PABLUM IN INFANT DIETS

City	Fluoride content, mgm.							
	4 month infant				12 month infant			
	Water (224gm.)	Milk (616gm.)	Pablum (7 gm.)	Total	Water (448gm.)	Milk (896gm.)	Pablum (35 gm.)	Total
Kitchener	0.036	0.049	0.084	0.169	0.072	0.072	0.420	0.564
Stratford	0.289	0.086	0.084	0.459	0.578	0.125	0.420	1.123

Presumably the larger part of the fluorine in Pablum is present as calcium salts. There appears to be some doubt as to the extent of absorption of fluorine in this form.

Studies on puppies (8) indicate that sodium fluoride is absorbed to a greater extent than fluoride fed as purified bonemeal or defluorinated phosphate. Rat experiments (10, 11, 18) indicate that, at low levels of intake, sodium fluoride and calcium fluoride are equally assimilable, and that there is a tendency for rats to adapt to relatively low levels of fluoride intake by excreting greater and greater proportions in feces and urine.

With a human adult subject, Machle and Largent (12) found that absorption was dependent upon the aqueous solubility of the fluoride salt and its state at the time of ingestion. With doses of 6 mgm. fluoride per day the following absorptions were found; sodium fluoride 97%; calcium fluoride in solution 95.5%; cryolite 77%; solid calcium fluoride 62%; bonemeal 37%. Some storage occurred at this level of intake.

McClure and coworkers (15) in balance studies on five young men confirmed the above findings as to absorption. They found that the elimination of fluoride via urine, feces, and perspiration is practically complete if the quantities absorbed do not exceed 4.0–5.0 mgm. per day.

Analyses made in this laboratory and elsewhere indicate that variations in the fluoride content of the diet as well as that of the water supply should be considered; especially is this true in the diet of infants. The absorption and retention of fluoride in growing humans has not been determined, but is under investigation by the authors.

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HUMIN FORMATION DURING WHEAT GLUTEN HYDROLYSIS[1]

By C. V. Lusena[2]

Abstract

The effect of different amounts of starch and crude fat on humin formation during the hydrolysis of gluten prepared from a commercial flour depended on the acid/protein ratio, high ratios giving less humin nitrogen and less humin weight. The nitrogen content of humin was almost independent of the acid/protein ratio but increased with decreasing humin formation. Filtration time increased markedly with increasing purity of the samples. The color of the hydrolyzates varied slightly with impurities and acid/protein ratios.

Introduction

Crude gluten is used extensively in the preparation of protein hydrolyzates. Under industrial conditions the lower the starch content of the gluten the lower the amount of insoluble humin formed and, while 10% insoluble humin greatly increases the filtration time, 3% has practically no effect (3). The colloidal humin adversely affects the color of hydrolyzates and the hydroscopicity of dried products.

Humin formation is attributed to a reaction of tryptophan with carbohydrates (2) and it may be related to the "browning reaction" in which amino acids react with carbohydrates to form brown compounds. The formation of these compounds is affected by the concentration of the reactants (1).

The object of this investigation was to study the effect of different amounts of starch and crude fat on humin formation at atmospheric pressure under both analytical and industrial conditions of hydrolysis.

Materials and Methods

The flour used was a commercial first patent containing 12.8% protein. The crude gluten samples (Nos. 1 to 4) were prepared by the Shewfelt and Adams method (5) and the purified gluten samples (Nos. 5 to 8) by dispersion and purification as previously described (4). Samples No. 3 and No. 8 were ethanol extracted after preparation and Sample No. 7 was prepared from ether extracted flour. All samples were vacuum dried at 5° C. and pulverized in a Raymond mill. Total nitrogen, moisture, ash, starch, and crude fat were determined as previously described (4).

Portions of the eight gluten samples containing 0.6 gm. of nitrogen were suspended, in duplicate, in sufficient constant boiling hydrochloric acid to

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give acid/protein ratios of approximately 3, 10, and 30. These ratios were chosen because an acid/protein ratio of 3 approximates industrial practice and acid/protein ratios of 10 and 30 approximate analytical procedures. These suspensions of protein in acid were heated to boiling in half an hour and then refluxed in an oil bath for 24 hr. The hot hydrolyzates were filtered through Whatman No. 50 paper and filtering times were recorded. The humin residues were thoroughly washed with water, dried, and weighed. The nitrogen content of the dry material was determined. The filtered hydrolyzates were analyzed for total, amino, and ammonia nitrogen: the amino nitrogen was estimated by the Van Slyke procedure and the ammonia nitrogen by steam distillation after adjusting the pH of the hydrolyzates to 8.5–9.0 with sodium borate. Preliminary tests showed that arginine nitrogen was not distilled under these conditions.

The filtered hydrolyzates were diluted to 0.36 mgm. of nitrogen per ml., and their color intensities were compared with an Evelyn photoelectric colorimeter at 420 mμ. Ease of decolorization was tested as follows: the original hydrolyzates were diluted to 6.0 mgm. of nitrogen per ml. and mixed with 0.2% (W/V) "Nuchar" vegetable charcoal, heated for 2.5 hr. at 100° C. while shaking, and then immediately filtered and the color determined as before. Under these conditions the hydrolyzates retained sufficient color to permit comparisons.

Results and Discussion

Ammonia and amino nitrogen values were unaffected by the impurities in the samples. The average contents of ammonia, amino, and insoluble humin nitrogen in the hydrolyzates at the three acid/protein ratios are shown in Table I. Hydrolysis was more complete at the higher acid/protein ratios and the amount of insoluble humin nitrogen at the low acid/protein ratio was at least twice as great as at the higher acid/protein ratios. Apparently the formation of insoluble humin is affected by the concentration of materials during hydrolysis.

Detailed results, means of duplicates, are given in Table II. They show that the amount of humin nitrogen did not vary extensively between gluten samples at the low acid/protein ratio but declined at the higher acid/protein

TABLE I

THE EFFECT OF ACID/PROTEIN RATIOS ON NITROGEN FRACTIONS IN GLUTEN HYDROLYZATES

(Averages for eight samples)

Acid/protein ratio	Ammonia N, % of total nitrogen	Amino N, % of total nitrogen	Insoluble humin N, % of total nitrogen
3	21.4	67.2	5.2
10	22.1	73.7	2.6
30	22.3	75.3	2.0

TABLE II

EFFECTS OF IMPURITIES AND ACID PROTEIN RATIO ON THE HUMIN FORMED DURING HYDROLYSIS OF GLUTEN

Gluten samples			Acid/protein ratio	Insoluble humin N, % of total N	Insoluble humin wt., % of sample wt.	Nitrogen in insoluble humin, %	Filtering time, min.	Light transmission of hydrolyzates, %	
No.	Starch dry wt., %	Crude fat, dry wt., %						Original*	Decolorized**
1	35.4	5.4	30	2.7	4.9	2.8	18.5	32.0	—
			10	3.4	11.0	2.9	10.0	33.5	13.0
			3	5.9	18.6	3.3	5.0	47.5	41.7
2	15.1	6.1	30	2.6	3.6	5.0	16.5	39.0	—
			10	3.0	9.9	4.1	13.0	30.5	14.0
			3	5.6	13.4	5.3	10.5	38.5	29.0
3	16.1	—	30	2.0	4.1	7.0	15.5	33	—
			10	2.3	5.0	5.3	11.5	31	—
			3	5.3	8.8	6.5	60.0	41	—
4	2.1	7.4	30	2.0	2.6	6.2	18	42	—
			10	2.3	10.0	4.1	14.5	35.0	63.0
			3	5.6	13.3	6.4	25.5	41.5	40.5
5	0.1	7.0	30	1.9	2.8	5.4	21.5	42	—
			10	2.2	8.3	4.2	25.0	32	51.5
			3	5.9	13.3	6.9	44.0	33.0	8.5
6	—	7.6	30	1.7	2.4	5.9	24.5	48.5	—
			10	1.9	9.1	5.2	32.5	39	77.0
			3	5.6	12.2	7.3	52.5	33.0	6.0
7	—	1.2	30	1.6	1.4	9.4	14.0	47.5	—
			10	2.0	5.1	6.4	24.0	41.0	81.5
			3	5.5	8.8	9.6	32.0	45.0	—
8	—	—	30	1.3	1.5	15.9	14.0	55.5	—
			10	2.1	2.9	13.1	17.0	40.0	—
			3	4.7	6.6	11.8	44.0	35.5	—

*Measured at 420 mμ wave length and a concentration of 0.36 mgm. N/ml.
**Measured at 420 mμ wave length and a concentration of 6.0 mgm. N/ml.

ratios with increasing purity of the gluten samples. Apparently the greater amount of humin nitrogen formed under "industrial" conditions masked the differences due to varying levels of impurities in the gluten samples.

The weight of insoluble humin increased with decreasing acid/protein ratios irrespective of impurities. A comparison of the weight of insoluble humin in Samples 6, 7, and 8 shows the importance of the fat, particularly at the lower acid/protein ratios. Starch alone (Samples 3 and 8) also increased the weight of insoluble humin but not so much as fat alone. Samples 2, 4, 5, and 6 show that increasing the amount of starch from 0 to 15% in the presence of approximately 7% fat did not increase the amount of insoluble humin.

Conversely the nitrogen content of the humin increased greatly with increasing purity of the sample, particularly at the high acid/protein ratio. At this ratio the nitrogen content of humin of the purest sample (No. 8) was 15.9% (the same as the nitrogen content of protein) while at the low acid/protein ratio the nitrogen content of humin from the same sample was 11.8%. Therefore at the latter ratio a reaction that did not involve starch or fat impurities produced humin of a lower nitrogen content. (This was not due to the long hydrolysis time (24 hr.) because after eight hours similar results were obtained.)

At a low acid/protein ratio, less sticky and more finely divided humin was produced from the gluten samples containing starch and fat than from the purified samples. This apparently permitted faster filtration of the hydrolyzates obtained at the low acid/protein ratio. But at the high acid/protein ratio the filterability of the hydrolyzates from all samples was similar. At the low acid/protein ratio the fat extracted sample containing 16% starch (No. 3) had the longest filtering time. Apparently the humin formed in the presence of fat had a texture that facilitated filtration. The filtration time for hydrolyzates obtained at the different acid/protein ratios cannot be compared directly because different volumes were filtered.

No marked trends were found in color intensity of the hydrolyzates. Removal of fat did not markedly reduce the soluble humin formed. The color of the hydrolyzates after decolorization was lighter for the impure than for the pure samples at the low acid/protein ratio, but was markedly lighter for the purer samples at the high acid/protein ratio.

From a practical standpoint it may be concluded that at each acid/protein ratio the amount of protein lost in the humin is almost independent of the purity of the gluten. The lowest amount was lost at the highest acid/protein ratio; but high ratios are uneconomic. For operational convenience the gluten should contain starch and fat but starch contents above 15% lead to excessive loss of material as humin.

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THE EFFECT OF SODIUM SULPHATE ON THE ABSORPTION OF ACID DYES BY WOOL[1]

By Barbara Benson[2] and P. Larose[2]

Abstract

The sorption of the dye Orange II by wool has been determined at the boiling point in the presence of various concentrations of sulphuric acid and of sodium sulphate within the range usually found in practice. Some experiments were also carried out with hydrochloric acid and sodium chloride. It is shown that the results for any one acid and salt concentration can be represented by a simple relation which has the same form for all results. Although this relation has the form of an adsorption isotherm, it remains purely empirical at present. The salt effect is readily explained on the basis of the Donnan equilibrium. The effect of acid strength is to fix the saturation value for the dye.

Introduction

Although the absorption of acid dyes by wool has been the subject of numerous investigations, there appears to have been no systematic study made of the effect of sodium sulphate on the acid dyeing of wool. Various views have been expressed to explain the leveling action of Glauber's salt in the dye bath and its effect in reducing the amount of dye taken up by the wool, but lack of sufficient experimental data has made the choice of any one theory rather difficult.

Briggs and Bull (2) have carried out some experiments on the absorption of dyes in the presence of sodium sulphate, but the dye and acid concentrations were not maintained constant so that their data are not sufficiently extensive to permit an analysis of the salt effect. These authors regarded the salt as competing with the dye for adsorption on the wool. Bancroft (1) also explained the salt effect as one of competition with the dye.

Speakman and Clegg (18) measured the effect of sodium sulphate on the absorption of a large number of dyes but they were more interested in the leveling action of the dyes than on the amount taken up. All their tests were carried out with one concentration of acid and of dye.

Gilbert (5) determined the dye concentration necessary in a bath to give a fixed amount of absorbed dye at various temperatures in the presence of two different sulphate concentrations for one of the dibasic dyes. However, the author was interested in the affinity of the dye, and the experimental data are too limited to enable one to reach any decision on the effect of the sulphate on the amount of dye taken up by the wool.

The reduction in dye absorption when sulphate is present has generally been ascribed to the sulphate ion competing with the dye anions regardless

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of whether the adsorption theory or the chemical theory of dyeing was envisaged. Gilbert and Rideal (6) imply this in their explanation of acid absorption while Gilbert (5) states definitely that if there are more protons available than dye anions (general condition in dyeing) sulphate ions will be adsorbed appreciably although the affinity for wool might be low.

Skinner and Vickerstaff (16) in applying the Langmuir adsorption equation look on the salt as competing with the dye for the adsorption sites.

Lemin and Vickerstaff (12) also mention the displacement of dye anions by inorganic anions.

Goodall (9) refers to the competition between salt and dye but mentions also that the sulphate ion has a specific action of its own because the effect of chloride and phosphate ions appeared to be much less. However, in earlier papers (7, 8) he had resorted to the Donnan equilibrium to explain dye absorption and the reduction of dye take-up in the presence of salts. Elöd (4) also used the Donnan equilibrium concept to explain the influence of salts. Neale (14) attributes the effect of salts to the change in the charge on the fiber. According to his views the positive charge of the wool fiber is reduced in the presence of salts and the decreased charge results in a lower affinity for the negatively charged dye ion.

Peters and Speakman (15) rule out the possibility of undissociated salt formation between anion and the positively charged NH_3^+ group, and according to their views therefore there can be no competition between sulphate and dye anions for the wool. It will be shown in the discussion of our results that the Donnan equilibrium concept as applied by Peters and Speakman can explain the salt effect in reducing dye absorption. However, this does not rule out the possibility of the dye anion combining with the wool.

Method

The wool was the same as that used for the acid absorption experiments reported by Donovan and Larose (3). It was in the form of a fine worsted yarn that had been subjected to no chemical treatment except the scouring during manufacture. No attempt was made to purify the wool, but the wool was soaked overnight in distilled water, the pH of which was about 5.7. This did not remove all alkalinity in the wool, as later experiments showed, and the acid combining capacity was therefore higher than that of wool equilibrated at a pH $\sim$ 5.0. The small correction ($\sim$ 0.04 m.e. per gram of wool) however does not greatly affect the dye sorption, as later experiments with equilibrated wool have shown.

Samples weighing about 5 gm. in the conditioned state (65% R.H. and 22° C.) were used in every case and immersed in 250 ml. of the dye solution. Control samples were weighed from time to time for the determination of regain so that calculations could be made on the basis of dry wool. The

dye solution with the wool was boiled under a reflux condenser for 1½ hr. and any loss, determined by weighing before and after the experiment, made up by adding distilled water. This loss was generally 1 to 2 ml. only and negligible as regards acid content. The solution was brought again to the boil and the wool removed from the boiling solution, which was then allowed to cool to room temperature. Samples were removed from the cooled solution for determination of dye concentration and of pH. The pH was measured with a Model G Beckman pH meter calibrated at a pH 4.00 with a 0.05 *M* potassium acid phthalate solution. The dye content was determined by means of a Model 402EF Lumetron photoelectric colorimeter calibrated with solutions of known dye concentrations. Initial dye concentrations were known from the weight of dye used in preparing the solutions. The

TABLE I

SORPTION OF ORANGE II BY WOOL FROM SOLUTIONS OF 0.0156 *M* SULPHURIC ACID CONTAINING VARYING AMOUNTS OF DYE AND SODIUM SULPHATE

C_B = Concentration of dye in bath, in milliequivalents per liter.
C_F = Dye sorbed by wool, in milliequivalents per gram of dry wool.
The pH in columns 3, 6, 9, and 12 are the final pH values at equilibrium.

Initial pH											
1.72			1.68			1.70			1.72		
Salt concentration											
0.0			0.0031 *M*			0.0062 *M*			0.0124 *M*		
C_B	C_F	pH	C_B	C_F	pH	C_B	C_F	pH	C_B	C_F	pH
0.076	0.085	2.00	0.100	0.077	1.96	0.110	0.071	1.99	0.136	0.070	1.99
.111	.143	1.99	.117	.112	1.98	.140	.108	2.03	.184	.108	1.99
.121	.172	2.02	.159	.170	1.98	.180	.169	1.99	.215	.143	1.99
.143	.230	1.98	.198	.227	1.98	.238	.253	2.01	.234	.165	2.01
.169	.288	2.01	.231	.297	2.00	.267	.283	2.00	.290	.222	2.00
.209	.345	2.03	.288	.340	1.98	.309	.339	2.08	.326	.279	2.02
.243	.403	2.03	.277	.371	1.98	.377	.395	2.01	.392	.335	2.01
.280	.460	2.02	.303	.399	2.00	.383	.425	2.06	.429	.392	2.03
.324	.517	2.01	.324	.428	2.00	.429	.451	2.00	.490	.433	2.06
.368	.545	2.02	.348	.457	2.02	.452	.480	2.03	.540	.475	2.03
.429	.600	2.04	.372	.485	2.00	.492	.507	2.00	.588	.502	2.03
.508	.645	2.04	.413	.513	1.99	.600	.561	2.06	.638	.529	2.07
.598	.680	2.08	.440	.540	2.00	.685	.615	2.08	.668	.556	2.05
.674	.705	2.08	.493	.567	2.01	.785	.637	2.08	.770	.581	2.06
.839	.756	2.08	.546	.594	2.01	.889	.663	2.05	.836	.607	2.07
.991	.776	2.10	.592	.621	2.04	.977	.688	2.08	.900	.633	2.07
1.134	.798	2.09	.647	.647	2.04	1.102	.710	2.09	1.056	.653	2.08
1.318	.817	2.09	.725	.673	2.02	1.222	.733	2.06	1.176	.676	2.08
			.799	.698	2.02	1.340	.756	2.09	1.249	.702	2.08
			.907	.722	2.02	1.429	.766	2.04	1.407	.722	2.08
			1.024	.745	2.02	1.584	.773	2.04	1.550	.744	2.09
			1.188	.765	2.04	1.755	.792	2.04	1.766	.769	2.08
			1.350	.785	2.05	1.964	.809	2.05	2.281	.792	2.10
			1.565	.803	2.05						
			1.839	.816	2.06						

amount of acid and salt in the dye solution were determined by the quantity of standard solutions added to the bath. The dye used was Orange II in all experiments. Analysis showed that the dye contained about 4.0% of sodium chloride. Experiments with sodium chloride added to the dye bath showed that the small amount of chloride in the dye had little effect on the dye absorption. This was confirmed by experiments with some purified dye which gave results identical with those obtained with the unpurified dye, due allowance being made for the impurities. All results are reported on a basis of pure dye.

TABLE II

SORPTION OF ORANGE II BY WOOL FROM SOLUTIONS OF 0.0078 *M* SULPHURIC ACID CONTAINING VARYING AMOUNTS OF DYE AND SODIUM SULPHATE

C_B = Concentration of dye in bath, in milliequivalents per liter.
C_F = Dye sorbed by wool, in milliequivalents per gram of dry wool.
The pH in columns 3, 6, 9, and 12 are the final pH values at equilibrium.

Initial pH											
1.88			1.96			1.98			2.02		
Salt concentration											
0.00			0.0031 *M*			0.0062 *M*			0.0124 *M*		
C_B	C_F	pH	C_B	C_F	pH	C_B	C_F	pH	C_B	C_F	pH
0.082	0.085	2.49	0.113	0.071	2.55	0.065	0.026	—	0.168	0.068	2.61
.130	.141	2.51	.145	.111	2.57	.095	.039	—	.229	.106	2.63
.139	.171	2.52	.174	.145	2.57	.107	.054	—	.281	.139	2.63
.182	.228	2.55	.200	.167	2.59	.123	.071	—	.305	.161	2.64
.235	.284	2.54	.254	.224	2.60	.141	.081	—	.371	.217	2.65
.276	.341	2.58	.290	.281	2.64	.157	.089	—	.468	.271	2.69
.346	.397	2.61	.319	.309	2.62	.167	.110	—	.557	.325	2.76
.424	.452	2.63	.375	.336	2.62	.188	.120	—	.710	.388	2.75
.554	.504	2.68	.430	.392	2.65	.209	.137	—	.779	.416	2.78
.715	.554	2.71	.472	.414	2.65	.222	.160	—	.892	.454	2.75
.885	.604	2.83	.545	.430	2.69	.240	.165	—	.993	.479	2.76
1.035	.627	2.84	.633	.470	2.73	.257	.182	—	1.119	.501	2.82
1.265	.641	2.79	.678	.496	2.75	.276	.193	—	1.219	.525	2.81
1.552	.654	2.93	.706	.510	2.73	.296	.224	—	1.315	.531	2.82
			.797	.520	2.77	.322	.250	—	1.404	.544	2.83
			.860	.546	2.76	.341	.278	—	1.567	.564	2.85
			.930	.557	2.77	.349	.308	—	1.741	.583	2.86
			1.057	.564	2.78	.418	.316	—			
			1.142	.590	2.80	.444	.332	2.60			
			1.395	.609	2.82	.490	.359	2.63			
			1.565	.624	2.84	.604	.413	2.67			
			2.627	.682	2.90	.675	.438	2.64			
						.805	.461	2.73			
						.819	.490	2.72			
						.877	.520	2.69			
						1.090	.534				
						1.066	.545	2.75			
						1.294	.582	2.73			
						1.461	.602	2.77			
						1.733	.616	2.86			

Dye absorption was determined with three different strengths of sulphuric acid with and without sodium sulphate of three different concentrations. Two series of tests were also carried out in which the sodium sulphate was replaced by sodium chloride and in another series hydrochloric acid was used instead of sulphuric acid.

TABLE III

SORPTION OF ORANGE II BY WOOL FROM SOLUTIONS OF 0.0039 *M* SULPHURIC ACID CONTAINING VARYING AMOUNTS OF DYE AND SODIUM SULPHATE

C_B = Concentration of dye in bath, in milliequivalents per liter.
C_F = Dye sorbed by wool, in milliequivalents per gram of dry wool.
The pH in columns 3, 6, 9, and 12 are the final pH values at equilibrium.

Initial pH											
2.14			2.20			2.24			2.29		
Salt concentration											
0.00			0.0031 *M*			0.0062 *M*			0.0124 *M*		
C_B	C_F	pH	C_B	C_F	pH	C_B	C_F	pH	C_B	C_F	pH
0.115	0.083	3.38	0.151	0.069	3.38	0.177	0.067	3.39	0.257	0.074	3.40
.176	.138	3.43	.214	.107	3.42	.256	.104	3.48	.322	.100	3.38
.215	.166	3.46	.279	.139	3.44	.313	.137	3.44	.393	.126	3.45
.268	.193	3.50	.379	.187	3.52	.356	.158	3.52	.473	.151	3.46
.308	.221	3.53	.452	.212	3.57	.443	.183	3.55	.544	.177	3.48
.359	.247	3.50	.540	.237	3.62	.505	.209	3.55	.659	.200	3.52
.462	.271	3.48	.613	.262	3.68	.628	.232	3.59	.726	.226	3.57
.517	.298	3.63	.692	.270	3.72	.739	.255	3.67	.841	.249	3.60
.759	.313	3.80	.778	.282	3.72	.864	.277	3.72	.999	.270	3.68
1.001	.329	3.89	.943	.303	3.79	1.015	.298	3.75	1.185	.288	3.72
1.325	.339	3.75	1.083	.325	3.83	1.241	.315	3.78	1.399	.306	3.72
2.062	.357	4.12	1.322	.340	3.89	1.558	.325	3.86	1.640	.322	3.78
			1.843	.340	4.01						
			2.277	.342	4.04						

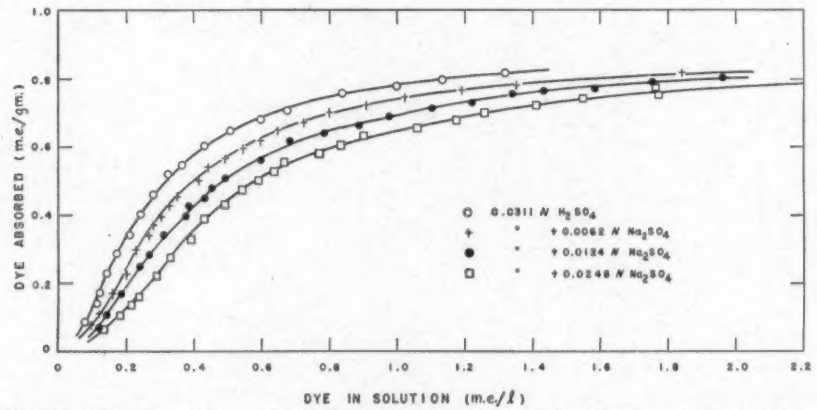

FIG. 1. *Absorption of Orange II in 0.0156 M sulphuric acid with and without sodium sulphate.*

Results

The results are given in Tables I–IV and are expressed in the form of absorption curves, in Figs. 1–4, where the number of milliequivalents of dye taken up by 1 gm. of wool are plotted against the residual concentration of the dye in the solution.

Each result represents the mean of three or four tests. Since most of the dye used is absorbed by the wool, any small error in the determination of the residual dye has little effect on the calculated amount of dye taken up by the wool, and the error shows up only along the abscissa, which represents the strength of the bath. The maximum deviation of any single determination from the mean was about 2% on the average, so that the error in the strength of the dye bath is not much more than 1%.

The error in the pH determinations is probably ±0.01 unit although a few of the determinations may be out by 0.02 unit.

TABLE IV

SORPTION OF ORANGE II BY WOOL FROM SOLUTIONS OF SULPHURIC ACID AND OF HYDROCHLORIC ACID IN THE PRESENCE OF SODIUM CHLORIDE

C_B = Concentration of dye in bath, in milliequivalents per liter.
C_F = Dye sorbed by wool, in milliequivalents per gram of dry wool.
The pH in columns 3, 6, 9, and 12 are the final pH values at equilibrium.

0.0078 *M* hydrochloric acid						Sulphuric acid					
						0.0078 *M*			0.0039 *M*		
Initial pH											
1.88			1.91			1.98			2.23		
Salt concentration											
0.00			0.0124 *M*			0.0124 *M*			0.0124 *M*		
C_B	C_F	pH	C_B	C_F	pH	C_B	C_F	pH	C_B	C_F	pH
0.015	0.089	2.29	0.026	0.088	2.44	0.101	0.083	2.60	0.131	0.082	3.50
.026	.177	2.33	.052	.176	2.47	.155	.170	2.60	.232	.165	3.55
.040	.236	2.44	.070	.234	2.50	.202	.227	2.63	.333	.219	3.62
.051	.295	2.43	.087	.293	—	.244	.284	2.68	.507	.268	3.73
.073	.353	2.53	.111	.351	2.54	.303	.340	2.68	.636	.291	3.79
.093	.412	2.58	.135	.409	2.63	.371	.396	2.69	.842	.308	3.89
.129	.469	2.61	.168	.467	2.66	.447	.450	2.76	1.045	.326	3.95
.165	.525	2.63	.227	.523	2.73	.558	.503	2.73	1.393	.336	4.04
.233	.582	2.73	.307	.578	2.81	.678	.556	2.77	2.260	.346	4.17
.355	.635	2.81	.468	.629	2.91	.795	.579	2.78	3.091	.357	4.25
.566	.682	2.98	.828	.678	2.92	.996	.598	2.84			
1.196	.706	3.03	1.167	.707	3.12	1.108	.620	2.88			
1.468	.719	3.10	1.465	.719	3.16	1.275	.642	2.88			
1.702	.736	3.22	1.774	.731	3.21	1.511	.657	2.91			

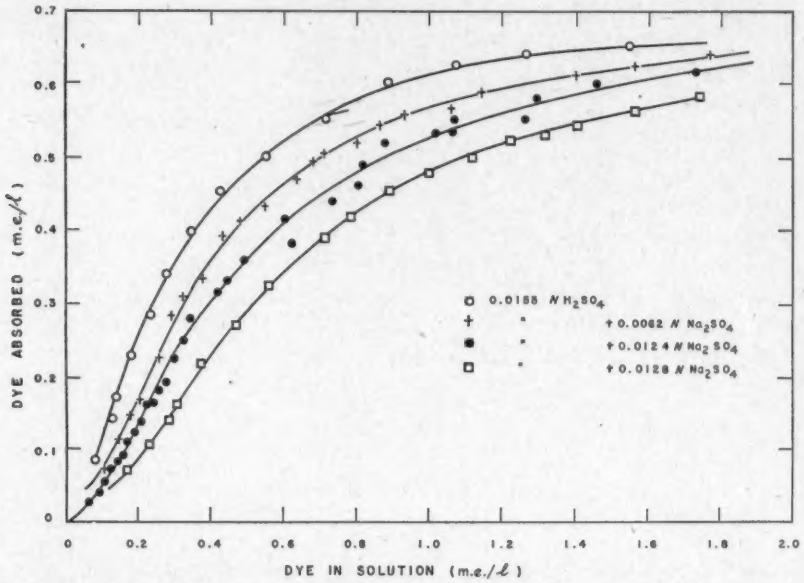

FIG. 2. *Absorption of Orange II in 0.0078 M sulphuric acid with and without sodium sulphate.*

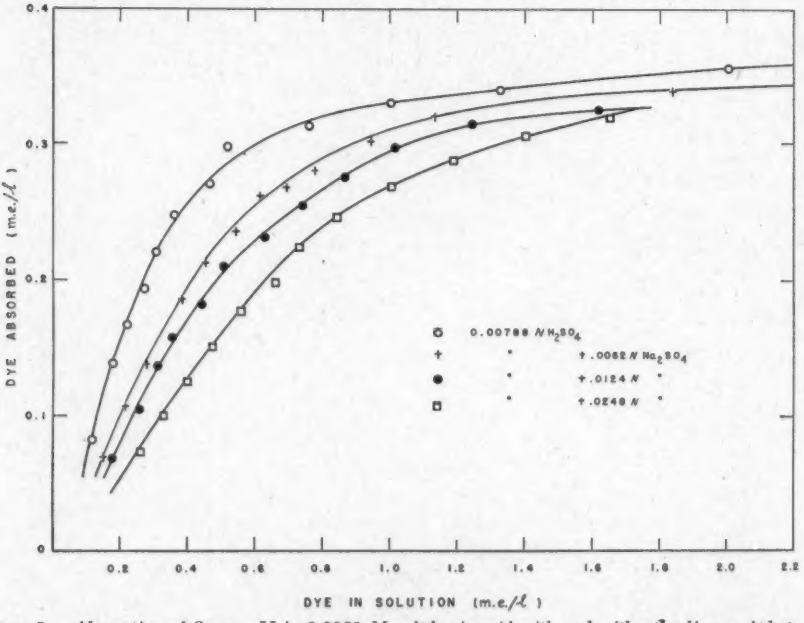

FIG. 3. *Absorption of Orange II in 0.0039 M sulphuric acid with and without sodium sulphate.*

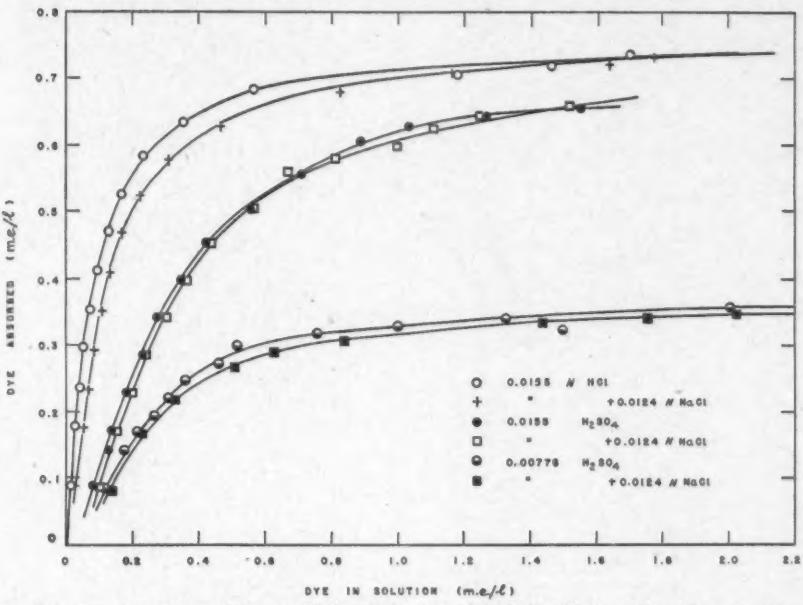

FIG. 4. *Absorption of Orange II in sulphuric and in hydrochloric acids with and without sodium chloride.*

Discussion

When the amount of dye sorbed is plotted against the dye bath concentration, the curves obtained all present the same general form irrespective of the acid or salt concentrations. This will become more evident when the equations for the curves are discussed. The similar shape for all curves immediately suggested that they could be made to coincide by appropriate changes in the abscissa and ordinate scales. It was indeed found possible to do this up to fairly high concentrations of the dye bath, but at the higher concentrations the curves diverge somewhat. Fig. 5 illustrates the three curves obtained for the three different acid strengths when the abscissa scale was changed to correct for differences in salt concentration, in order to bring the salt curves in coincidence with the curves obtained with the acid alone. The factors by which the abscissae were multiplied are given in the following tabulation.

Acid concentration, *M*	Salt concentration		
	0.0031 *M*	0.0062 *M*	0.0124 *M*
0.0039	0.645	0.532	0.420
0.0078	0.763	0.624	0.476
0.0156	0.781	0.654	0.524

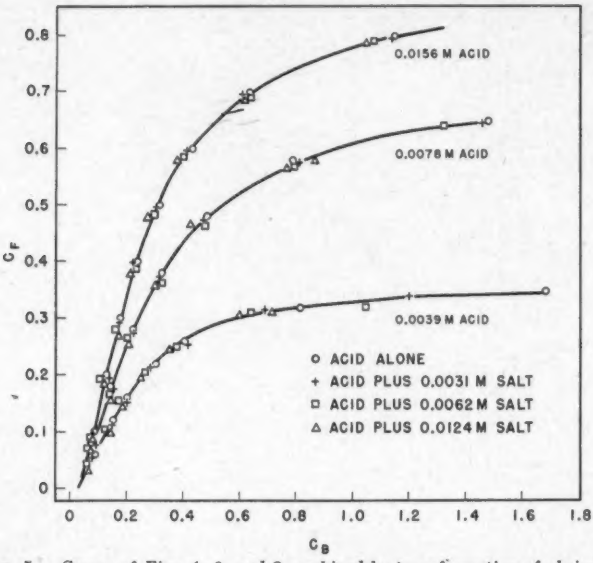

FIG. 5. *Curves of Figs. 1, 2, and 3 combined by transformation of abcissae.*

In a similar fashion but by changing the scale of the ordinates, these three acid curves can be combined in turn to give the curve shown in Fig. 6. The 0.0039 *M* and 0.0078 *M* acid curves were made to coincide with the 0.0156 *M* curve by multiplying the ordinates by 2.24 and 1.30 respectively. It will be seen that all points thus fall closely on one curve except for the highest concentrations of dye where the divergence is probably greater than the experimental error. Although this method of combining the curves is purely empirical, a study of the equations of the curves will show why this is possible.

In view of the application that has already been made of the Gilbert and Rideal (6) theory to explain the acid and dye sorption by wool, we might first examine our results in the light of the same theory.

The Gilbert and Rideal theory was applied by Meggy (13) to the results he obtained with the pure dye acid of Orange II and by Lemin and Vickerstaff (12) to the results obtained with a number of other acid dyes. These authors claimed good agreement between their results and the theory which they used to calculate the affinity of the dyes for wool. The absence of salts in these examples simplifies the problem, and the test of the theory is more direct.

When sulphate and sodium ions are present in the bath we have, following the reasoning of Gilbert–Rideal:

$$RT \ln \frac{\theta_D}{1-2\theta_{SO_4}-\theta_D} = RT \ln D + \psi F - \Delta\mu_D$$

and

$$RT \ln \frac{\theta_H}{1-\theta_H-\theta^{Na}} = RT \ln H - \psi F - \Delta\mu_H,$$

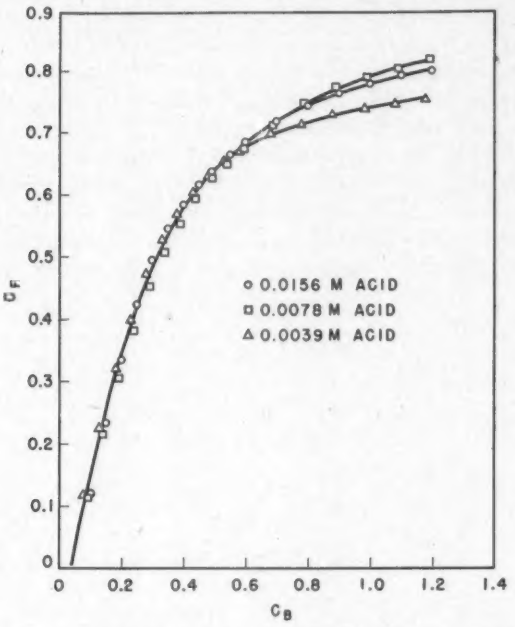

FIG. 6. *Curves of Fig. 5 combined by transformation of ordinates.*

where θ_D, θ_{SO_4}, θ_H, θ_{Na} represent the fractions of the available sites occupied by the respective ions indicated as subscripts. D and H are the concentrations of dye anions and hydrogen ions respectively in the solution, F is the Faraday, ψ the potential around the sites available to the ions, and $\triangle\mu$ the change of chemical potential of the ion shown by the subscript on adsorption.

If we assume that θ_{Na} is negligible and write $1-\theta_{2SO_4}-\theta_D=1-\theta_H$, we get

$$\ln \theta_D = \ln D + \ln H - \ln \frac{\theta_H}{(1-\theta_H)^2} - \frac{(\triangle\mu_D + \triangle\mu_H)}{RT}.$$

If θ_H is constant, then plotting log θ_D or log C_F, where C_F represents the amount of dye sorbed by the fiber, against log D + log H should give a straight line of slope 1. Our results for the 0.0078 M acid with no addition of sodium sulphate have been plotted in this way in Fig. 7. Only the lower points lie reasonably well on a straight line. Moreover the slope of the line is greater than 1. Similar curves are obtained with the other results. It is possible, of course, that θ_H is not constant but becomes greater as the concentration of dye in the bath increases. Since this would make the term $\ln \frac{\theta_H}{(1-\theta_H)^2}$ larger, particularly at the higher concentrations, it may have the tendency to straighten out the curve at the upper points. It would be sufficient in

this case for θ_H to increase from the initial value of 0.80 for the low dye concentrations to 0.87 for a dye concentration of 1.3 m.e. per liter in order to give a straight line all the way. The fact that the pH of the solution increases as more dye is added to the solution and sorbed would indicate that θ_H does increase with increasing dye concentration. The change of pH with increasing dye concentration may also be partly due to a buffer action of wool decomposition products. The possible effect of decomposition on the dye sorption has not been overlooked, but all indications are that it is negligible. Smith and Harris (17) found the same amount of dye sorbed at 49° C. as at the boiling point after reducing the temperature to decrease chemical

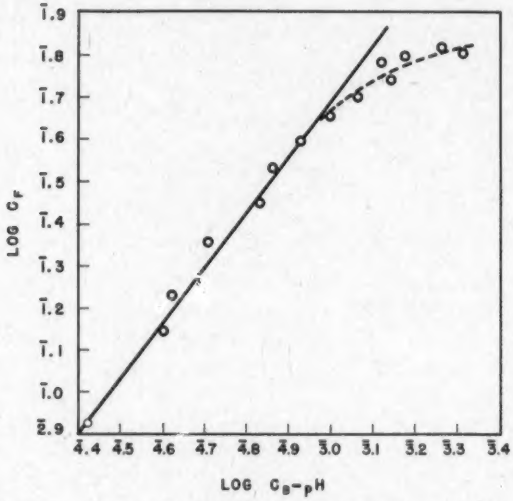

FIG. 7. *Relation between log C_F and log $C_B - pH$ as a test of the Gilbert and Rideal theory.*

action. Other experiments that we have carried out, to be published later, also tend to show that the effect of decomposition of the wool is small. These experiments support the view that θ_H increases with increasing dye concentration. Goodall and Hobday (10) also concluded from their tests that the amount of wool damage resulting from a three hour treatment with boiling 0.01 *N* hydrochloric acid was negligible. This would mean that the amount of total acid sorbed by the wool depends not only on the hydrogen ion concentration but also on the anion concentration. It is possible, however, that the apparent higher values of θ_H obtained with increasing sorption of dye is due to adsorption of undissociated dye or acid molecules. Quantitative analysis of the results, however, is not possible until one takes into account the Donnan equilibrium effect and knows more of the swelling properties of the wool in the presence of the dye. It would be futile, therefore, to speculate further on this point but it might also be recalled that

Briggs and Bull claimed to have obtained a greater acid sorption in the presence of dye than with the acid alone.

The significance of the Donnan equilibrium in the mechanism of acid sorption was well shown by Peters and Speakman (15), but its importance may be further emphasized by taking the data of Lemin and Vickerstaff (12) on the sorption of Naphthalene Orange G and of Solway Ultra Blue B, in the presence of hydrochloric acid and sodium chloride. These authors used the Gilbert and Rideal concept to explain the effect of the chloride ion concentration on the sorption of the dyes. They assumed that chloride ions displace some of the dye on the fiber according to the reaction

$$W.D + Cl^- \rightleftharpoons W.Cl + D^-,$$

although in the earlier part of their paper, in the calculation of the affinities of the various dye anions, they assumed that the chloride ion had negligible affinity for wool. However, it is not necessary to assume any affinity of the chloride ion to explain their results.

The Donnan equilibrium gives $[D^-]_i = \lambda [D^-]_0$, where $[D^-]_i$ and $[D^-]_0$ are the dye anion concentrations in the fiber and in the solution respectively and $\lambda = 1 + \frac{C_1}{C_2 + C_3}$, C_1 being the concentration of the protein ion ($R.NH_3^+$), C_2 that of the acid in the bath, and C_3 that of any other electrolyte in the bath, in this case sodium chloride.

If we assume a figure of 32 cc. per 100 gm. of wool, as given by Peters and Speakman (15), for the volume swelling of wool at a pH of 2.0 and 51 m.e. per 100 gm. of wool as the number of wool ions $- RNH_3^+$, we have $C_1 = 1.6$, $C_2 = 0.001$, and C_3 varying from 0.01 to 1.00. From this we may calculate λ and thus $[D^-]_i$ with the following results:

C_3	λ	$[D^-]_i \times 10^4$		
		Naphthalene Orange G		Solway Ultra Blue B
		$\theta_D = 0.271$	$\theta = 0.403$	$\theta = 0.760$
0.01	81	6.5	7.8	—
0.02	54.3	5.5	8.5	—
0.05	27.7	4.2	8.3	1.04
0.10	15.5	4.9	10.3	1.18
0.15	11.0	4.6	9.2	1.17
0.20	8.6	4.9	9.5	1.25
0.25	7.2	4.7	10.4	1.23
0.50	4.1	4.9	12.1	1.01
1.00	2.6	—	8.5	—
	Mean	5.0	9.4	1.15
	$\frac{\theta_D}{1 - \theta_D}$	0.37	0.67	3.17

These figures show that $[D^-]_i$ is sensibly constant and that it is not necessary to introduce the chloride ion displacement to explain the constancy of θ_D. It will be noted that the ratio of $\frac{\theta_D}{1-\theta_D}$ to $[D^-]_i$ is practically the same for the two series of tests with Naphthalene Orange G. This is what might be expected if the sorption takes the form of a regular Langmuir adsorption or if it proceeds according to a mass action law, e.g., $W^+ + D^- \rightleftharpoons WD$, where W^+ stands for the RNH_3^+ ion concentration in the wool. Moreover this leads to values of $(\Delta\mu_{D_1} - \Delta\mu_{D_2})$, the difference in affinity of the two dyes, of around 1.6 − 1.8 kgm-cal. which is in better agreement with the differences obtained in the other experiments carried out by Lemin and Vickerstaff (12) in which the sorption in mixtures of the dyes was determined.

We have also applied the Langmuir isotherm to our data with good results provided that certain assumptions are made. The Langmuir treatment for adsorption leads to an equation of the form $\frac{C_B}{C_F} = \alpha + \beta C_B$, where C_B and C_F represent the concentrations of the dye in the solution and in the fiber respectively; α and β are constants. This is the equation used by Skinner and Vickerstaff (16) to account for the adsorption of some acid dyes by wool.

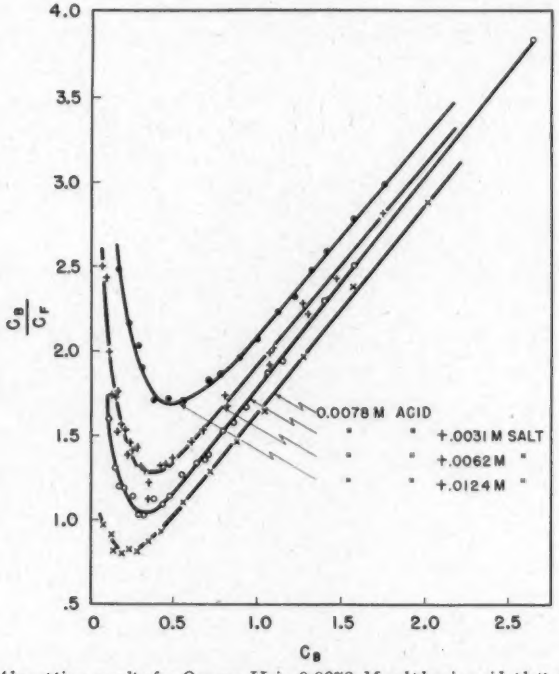

FIG. 8. *Absorption results for Orange II in 0.0078 M sulphuric acid plotted as a test of the expression* $\frac{C_B}{C_F} = \alpha + \beta C_B$.

The equation becomes $\frac{C_B}{C_F} = \alpha + \beta C_B + \gamma C_A$ when another ion "A" competes with the dye anion for the sites on wool, C_A being the concentration of the competing anion in solution and γ a constant. We have assumed that there is no such competition between the dye anions and the sulphate or chloride ions in our experiments and that the term C_A can be disregarded.

We have plotted one set of our results in Fig. 8 according to the first equation given above. A straight line relation is obtained only for the higher values of C_B but, since C_B varies more rapidly than C_F, and C_F tends to become constant for high concentrations, a straight line in this region does not necessarily indicate agreement with a Langmuir isotherm. Skinner and Vickerstaff (16) obtained the same general form of curve from their results with Disulphine Blue.

We have found, however, that all experimental points lie in a straight line corresponding to the equation $\frac{C_B{}^n}{C_F} = \alpha + \beta C_B{}^n$, where n is a constant that lies between 1 and 2 for any one set of results. We can, therefore, write $\frac{\theta_D}{1-\theta_D}$ proportional to $C_B{}^n$ and determine n by plotting log $\frac{\theta}{1-\theta}$ versus log C_B, choosing the best value for the maximum combining capacity of wool. Since small variations in this value do not change the slope of the plot appreciably,

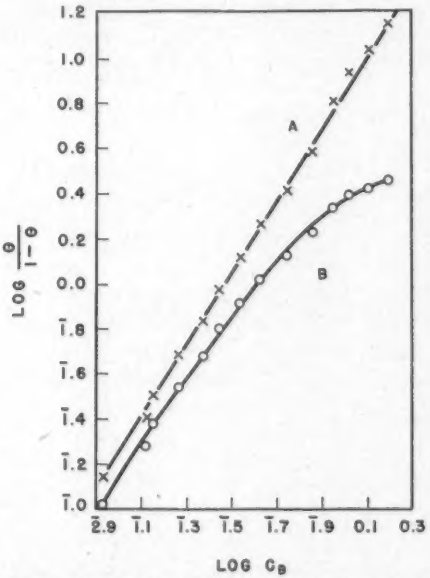

FIG. 9. *Absorption results with the 0.0078 M sulphuric acid without salt plotted as a Langmuir isotherm. Curve A, using 0.70, and curve B, using 0.88, as the maximum combining capacity of the wool in milliequivalents per gram.*

it was sufficient to take approximate values from the experimental curves (Figs. 1–4). Fig. 9 is an example of this plot for the 0.0078 *M* acid without salt. Having obtained n in this way, we plotted $\frac{C_B{}^n}{C_F}$ versus $C_B{}^n$, and for every set of results a good fit to a straight line was obtained. Fig. 10 gives such a plot for hydrochloric acid and for sulphuric acid in the presence of

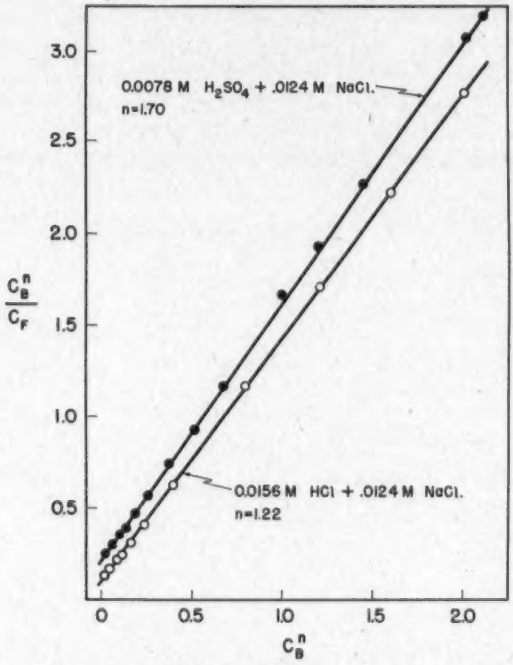

FIG. 10. *Absorption results for 0.0078 M sulphuric acid and for 0.0156 M hydrochloric acid with sodium chloride plotted according to the modified isotherm* $\frac{C_B{}^n}{C_F} = \alpha + \beta C_B{}^n$.

sodium chloride. The inverse slope of the line should correspond to the saturation value of the wool under these particular conditions. Table V gives the various values of n and C_F (max.) obtained from the curves and includes results obtained with wool equilibrated to a pH 5.4 before sorption.

The change in the amount of dye sorbed when sodium sulphate is added to the dye bath can be explained satisfactorily by the Donnan effect although an exact treatment is impossible with present data. In calculating λ, the ratio of dye anion concentration in the internal phase to that in the bath, we have followed a procedure very similar to that used by Peters and Speakman (15) to calculate the hydrogen ion concentration within the fiber in equilibrium with sulphuric acid solutions. Application of the Donnan

TABLE V

CALCULATED VALUE OF n AND OF C_F (MAX.) $= \frac{1}{\beta}$ IN THE EXPRESSION

$$\frac{C_B{}^n}{C_F} = \alpha + \beta C_B{}^n$$

Acid	Salt	n	C_F (max.)
0.0154 M H_2SO_4	None	1.66	0.85_0*
0.0156 M H_2SO_4	None	1.79	0.85_0
"	0.0031 M Na_2SO_4	1.87	0.84_8
"	0.0062 M "	1.81	0.83_4
"	0.0124 M "	1.84	0.83_3
0.0084 M H_2SO_4	None	1.42	0.77_0*
0.0077 M H_2SO_4	None	1.55	0.67_8*
0.0078 M H_2SO_4	None	1.58	0.70_0
"	0.0031 M Na_2SO_4	1.62	0.69_0
"	0.0062 M "	1.69	0.69_0
"	0.0124 M "	1.71	0.67_3
"	0.0124 M NaCl	1.70	0.70_1
0.0039 M H_2SO_4	None	1.65	0.39_9*
0.0039 M H_2SO_4	None	1.66	0.36_4
"	0.0031 M Na_2SO_4	1.68	0.36_1
"	0.0062 M "	1.70	0.36_7
"	0.0124 M "	1.81	0.36_4
"	0.0124 M NaCl	1.58	0.35_5
0.0156 M HCl	None	1.12	0.76
"	0.0124 M NaCl	1.22	0.76

**These results were obtained with equilibrated wool and with purified dye.*

equilibrium to the system wool–dye–acid leads to an expression

$$\frac{a_H - a_D}{v} = \frac{\lambda^3 - 1}{\lambda}(D + U) + \frac{\lambda^3 - 1}{\lambda} \cdot 2X$$

from which λ can be calculated if the other quantities are known.

a_H and a_D represent the number of protons and dye anions respectively combined with the wool.

v is the volume of the internal phase.

D, U, X are the concentrations of the dye, hydrosulphate, and sulphate anions respectively in the bath.

The above expression is only an approximation since all activity coefficients have been taken as 1. The number, a_H, of combined hydrogen ions was assumed constant for any one acid strength and equal to the maximum combining capacity of the wool for that acid, while a_D was chosen arbitrarily as 0.50 m.e. per gram of wool for the 0.0156 M and 0.0078 M acids, and 0.25 m.e. for the 0.0039 M acid. The values of D are those found experimentally for the chosen values of a_D while U and X were calculated using the dissociating constant 0.0124 for the HSO_4^- ion. The values of v were those given by Peters and Speakman for sulphuric acid of corresponding strengths. The swelling of wool at the boiling point may be quite different from that at ordinary room temperature for which Peters and Speakman give their values of v but there are no available data known to us from which

the values of v at the boiling point could be calculated directly. Moreover Hall (11), by extrapolation of data furnished by Speakman, Stott, and Chang (19), calculated that the swelling at the boiling point was only about 1% greater than at 20° C. but our own calculations give a difference of about 5% for the fine wool. It may also be pointed out that using a different value of v would lead to different values of λ but the ratio between them would remain the same, so that our argument would not be affected by this change. A small amount of salt present in the dye used will also affect the calculations of λ.

With the calculated values of λ, the concentration of dye, D_i, in the internal phase was determined. The results are given in Table VI.

TABLE VI

CALCULATED VALUES OF λ AND D_i (MILLIEQUIVALENTS PER LITER) FOR THE SULPHURIC ACID SOLUTIONS WITH AND WITHOUT SALT

Sodium sulphate concentration	Acid strength					
	0.0039 *M*		0.0078 *M*		0.0156 *M*	
	λ	D_i	λ	D_i	λ	D_i
No salt	8.1	0.304	9.2	0.291	8.4	0.451
0.0031	5.7	0.331	7.8	0.308	6.3	0.440
0.0062	4.7	0.328	6.3	0.338	5.4	0.472
0.0124	3.6	0.305	5.7	0.331	4.3	0.474

For any fixed value of dye sorbed, D_i should be constant provided the activity coefficient remains the same. Although the calculated values given in Table VI for any one acid strength show some variations, these are irregular and not unduly large in view of the number of assumptions that had to be made. There seems little doubt, however, that the effect of the sulphate ion on the sorption of the dye can be accounted for purely by the Donnan concept, and there is no need to postulate competition between sulphate and dye anions. The difference in dye sorption resulting from the addition of sodium chloride to a hydrochloric acid solution of the dye can also be accounted for on the basis of the Donnan effect. The smaller effect of the sodium chloride addition to the sulphuric acid solution is readily explained in the same way. Here the sulphate ion concentration is the predominating factor in determining λ, and addition of sodium chloride does little to disturb this. The latter enters only in the monovalent ion term $\frac{\lambda^2-1}{\lambda}(D + U + \mathrm{Cl})$ in the expression given above, and this term has little effect on λ in comparison with the other which contains X, the concentration of the sulphate ion.

With the known equations of the different experimental curves, it is now possible to explain the transformations carried out earlier and to show why the various curves could be made to coincide.

With any one acid strength, we have a maximum combining capacity of the wool for the dye which appears to be practically the same irrespective of the sulphate concentration (within the limits studied). We can therefore write for any one value of C_F

$$\frac{(C_B')^n}{C_F} = a' + \beta(C_B')^n \qquad \frac{(C_B'')^n}{C_F} = a'' + \beta(C_B'')^n$$

for two different dye concentrations.

By division this gives $\frac{C_B'}{C_B''} = \left[\frac{a'}{a''}\right]^{1/n}$.

Since a', a'', and n are constant, the ratio C_B'/C_B'' should also be constant as we had found arbitrarily from the curves.

To correct for the difference in acidity, where ordinates corresponding to the same abscissa C_B were multiplied by a factor, we have:

$$\frac{(C_B)^{n'}}{C_F'} = a' + \beta'(C_B)^{n'} \qquad \frac{(C_B)^{n''}}{C_F''} = a'' + \beta''(C_B)^{n''}$$

which leads to

$$\frac{C_F'}{C_F''} = \frac{\beta''}{\beta'}\left[\frac{(C_B)^{n'}\ a'\ a'' + (C_B)^{n'}\ (C_B)^{n''}\ a'}{(C_B)^{n''}\ a'\ a'' + (C_B)^{n'}\ (C_B)^{n''}\ a''}\right].$$

Now the quantities within the brackets are of the same order of magnitude and n'' is generally smaller than n' when a'' is greater than a', so that the bracketed term is not very different from 1 and

$$\frac{C_F'}{C_F''} \simeq \frac{\beta''}{\beta'} \simeq \text{Constant},$$

which again explains the procedure followed earlier. It is readily seen also why this should break down at the higher values of C_B, where $(C_B)^{n'}$ becomes quite different from $(C_B)^{n''}$.

There may be several ways of explaining a coefficient of n greater than unity in the expression $\frac{\theta_D}{1-\theta_D} = KC_B{}^n$. If the amount of dye sorbed is dependent on θ_H as well as on C_B, as recent results obtained in this laboratory indicate, then $\frac{\theta_D}{1-\theta_D}$ should not be directly proportional to C_B but would increase more rapidly. However it is not possible at this time to give quantitative expression to this relation.

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THE MEASUREMENT OF THE HEAT OUTPUT FROM RADIANT HEATING PANELS ON A LABORATORY SCALE[1]

By Frederick Lipsett[2]

Abstract

The use of radiant heating panels 2 ft. square for obtaining data on heat outputs for design purposes, instead of panels about 15 ft. square, would save much time and expense. A miniature panel heating system was constructed and gave the desired data. For ceiling panels the method has the advantage of eliminating convective heat output. This is discussed in detail.

A. Introduction

In the design of ceiling panels for space heating, the most important datum is the amount of heat that can be obtained from each square foot of panel surface under given conditions. Several methods have been suggested by which this datum may be obtained (1, 4, 7). For instance, Raber and Hutchinson (7) give comprehensive methods of analyzing the flow of heat in a panel heated room, and from their work the heat output from a certain type of panel for a given set of conditions may be found if the "conductance" of the panel is known. For specific types of panels, Adlam (1) gives a number of graphs from which it is possible to compute the heat output from the panels for given conditions. According to Giesecke (4) the heat output from any panel can be calculated from the exterior surface area of the pipes within the panel and the temperature difference between the water in the pipes and the air in the room. It has been found, however, that these different methods do not always give the same results, and for many types of installations are not applicable at all. Hence the designer is often at a loss to know which method is best for his particular job and sometimes he is left with no method whatever.

There is a need, therefore, for some method by means of which the heat output from ceiling panels can be measured, so that accurate information may be obtained for a great variety of panels and so that the heat outputs predicted by the different authors may be compared with the measured values. Unquestionably, this problem could best be solved by measurements on full-scale installations in dwellings and, ultimately, for at least a few types of panels such measurements must be made. Measurements on a full scale, however, are very expensive and to test all types of panels under all conditions of operation would require a very lengthy research program. In full-scale installations the determination of heat output is difficult and the measurements become very complex. If, therefore, a method could be devised by

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which the heat output from panel heating installations could be obtained from measurements made in the laboratory on small representative sections of the panel, much trouble and expense would be obviated.

In considering such experiments it must be borne in mind that, notwithstanding the fact that such installations are generally known as radiant heating panels, heat is given off from a ceiling panel not only by radiation but also by convection and conduction. If we are to attempt to calculate the heat output obtained from ceiling panels in a dwelling from data obtained from measurements made on a small scale in a laboratory, we must know the effect of size on the three mechanisms of heat transfer. In this paper we shall describe some measurements made on a small panel and shall indicate how it is possible to correlate these measurements with the output from panels of full size.

B. Description of Experiment: Apparatus: Method of Measurement

Description of Experiment

The datum required for the competent design of a ceiling heating panel is the amount of heat that will be "radiated" to the room beneath by 1 sq. ft. of ceiling. The spacing and size of pipes and the temperature of the water are given. The problem is, knowing the latter, to be able to obtain the former for any given installation. To find, therefore, the relation between the quantities given (construction and temperatures of panel) and the output of heat it is necessary to design an experimental arrangement whereby the heat output can be measured. In the present experiment a miniature panel heating system was constructed and the output per unit area of a small test panel was measured by means of a cubical variation of a standard heat meter. A known area of the panel was enclosed by a cubical box (that is, the surface of the panel formed one side of the box) so that the heat from the panel was given off to the box. The heat then escaped through the walls of the box to a colder exterior. The walls of the box were constructed of material whose conductivity was known and the temperature drop across the walls was measured by thermocouples; thus, it was possible to measure the heat given off by the panel. The heat given off by the panel under the conditions of the experiment having been obtained in this way, it is now necessary to show what relation the heat output under such controlled experimental conditions bears to the output in a full size installation.

Heat will be given off from the surface of any ceiling panel by radiation, convection, and conduction. The heat output by radiation depends on the surface temperature and emissivity not only of the radiating surface but also of the surfaces that are receiving the radiation, and in addition it depends on the geometrical arrangement of the radiating and absorbing surfaces. The transmission of heat by radiation has been extensively studied and a theory that satisfactorily explains the measured results has been formulated.

If we are to be able to transpose results obtained on small panels to large panels we must know the effect of size on the heat transfer by radiation. The results of J. R. Carrol, Jr. (2, 3), which give the amount of heat radiated from a full scale panel when the temperature of the radiating plaster, the temperature of the air, and mean radiant temperature of the room are known, can be used to correlate the heat transfer by radiation from the small panels with that from full scale application. It must be realized that to use Carrol's results the temperature of the plaster must be known and the experiment is designed to supply the link between plaster temperature and the temperature of water in the pipes.

In addition to the heat given off by radiation, there is also a transfer of heat from the panel to the air by convection and conduction. In a full-scale room the heat that is transferred by true gas conduction (that is, from molecule to molecule without movement of the gas as a whole) is very small and we can combine the heat transferred by these two mechanisms under one designation, convection. The transfer of heat by convection from a heated surface to a gas depends upon the movement of the gas, and this movement may arise from many causes. In the heat transfer downwards from a heated panel the temperature differences arising from the panel would not in themselves start convection currents in the gas since the warm layers of air would be uppermost. In any room, however, there will be other factors such as cold walls or windows, air infiltration, or the movement of people, any one of which would set the air in motion. There will, therefore, be a transfer of heat by convection which it is impossible to estimate accurately.

In the heat transfer from a small-scale panel to a box as outlined above, the amount of heat transferred by convection would be very small indeed. With the temperature of the walls of the box established solely by the heat flow from the panel itself there would be no tendency for convection currents to be set up and the heat transfer would be almost completely by radiation. The heat meter box type does, therefore, give a method by which the amount of heat radiated from unit area of the ceiling can be measured. Since accurate measurements of the surface of the box can be made and since the geometry is such that the radiation laws can easily be applied, this gives us a method of establishing the amount of heat radiated per unit area of ceiling under known values of mean radiant temperature of the surroundings.

In this paper it is shown that the total heat transferred is, in fact, equal to that which would be transferred by radiation alone from the same area of a ceiling in a full-scale application. The methods used here do, then, offer a means of measuring the output from panel heating installations on a laboratory scale.

Apparatus

The arrangement of the apparatus is shown schematically in Fig. 1 and photographs are reproduced in Figs. 2*A*, 2*B*, and 2*C*. The test panel repre-

sents a radiant heating ceiling panel and it is so placed in the apparatus that it separates the top chamber, maintained at a fairly warm temperature, from the bottom chamber, maintained at a lower temperature. The top chamber corresponds to the room above the ceiling panel in the full-scale installation, the heat-meter box to the room to which the panel delivers heat,

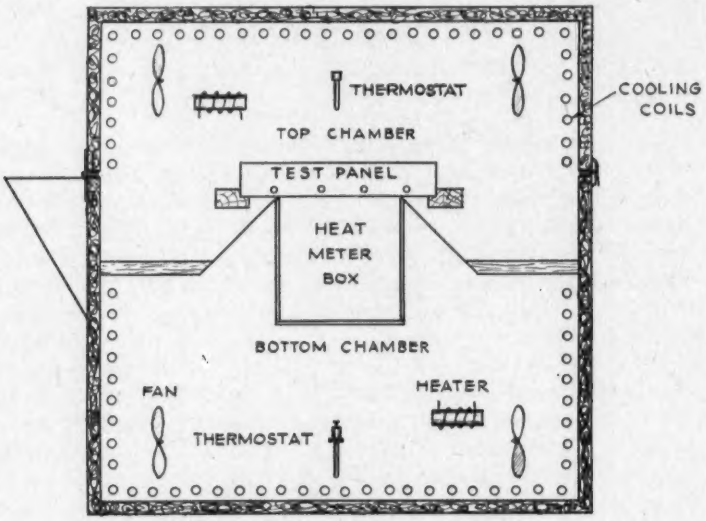

FIG. 1. *Schematic cross section of apparatus.*

and the bottom chamber to the outside atmosphere. The heat-meter box is placed against the surface of the panel so that the heat from a known area of the panel flows through the box to reach the bottom chamber.

The panel used in these experiments is shown in cross-section in Fig. 3. To supply the heat, water whose temperature was carefully controlled was

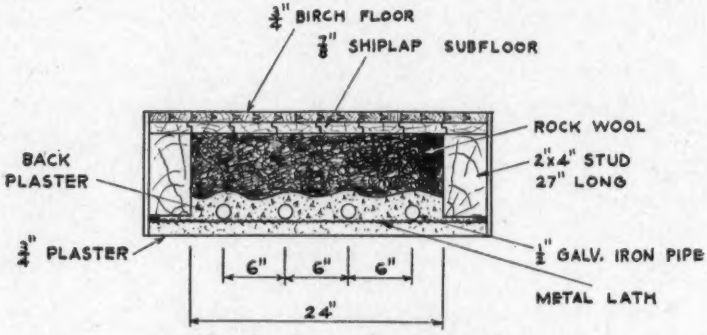

FIG. 3. *Cross section of test panel.*

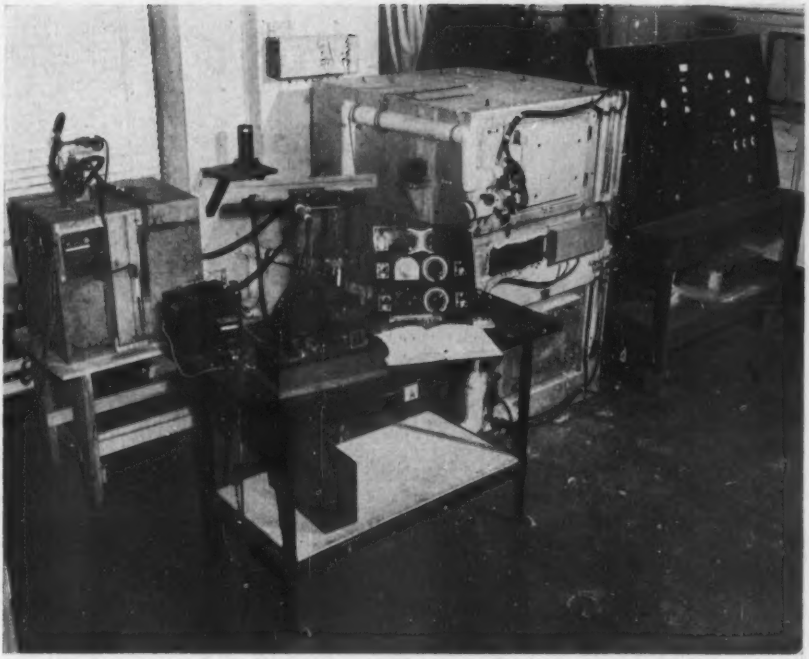

FIG. 2A. *General view of the apparatus showing, left to right: constant temperature tank for hot water; table with pyrometric apparatus, including thermocouple swilchboard; constant temperature chambers in which test panel was placed; and electrical panel with controls for voltage regulators for auxiliary heaters.*

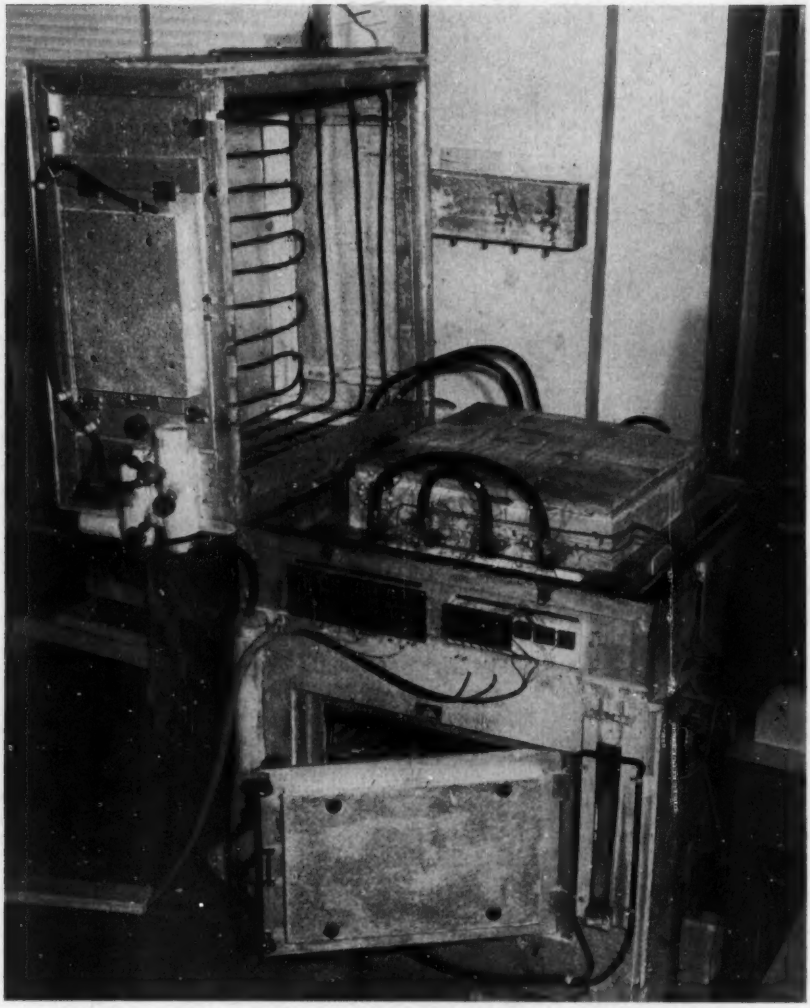

FIG. 2B. *Constant temperature chambers with top chamber raised to show panel in position for testing. The terminal plate is for copper thermocouple leads and zone box (cover removed) for constantan thermocouple leads. The manometer indicates the flow of refrigerant through the chamber cooling coils.*

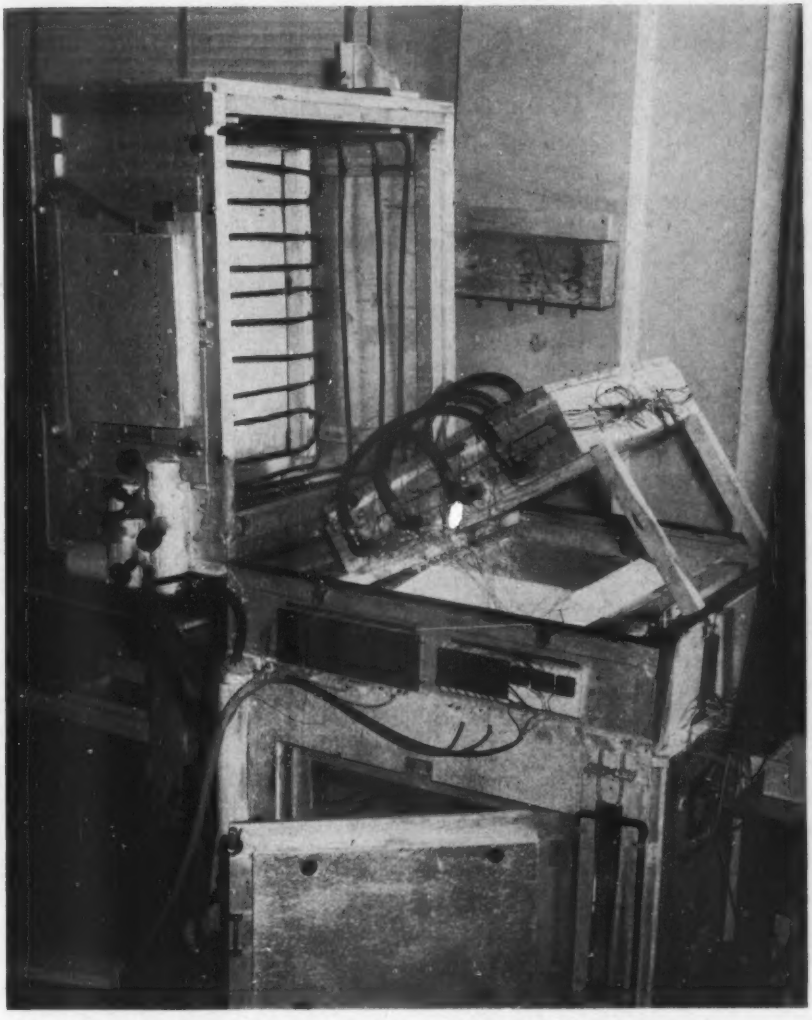

FIG. 2C. *Same as Fig. 2B but with test panel raised to show heat meter box.*

circulated through the pipes. In order to prevent the loss of heat from the ends and sides of the panel, electrical heating elements were wound on the ends of the pipes and were placed on the sides of the panel. It was found, however, that these auxiliary heaters had no effect on the measurements and they were seldom used.

During a test the top and bottom chambers were cooled by coils through which a refrigerated liquid was circulated. The temperatures were held constant by means of electrical heaters controlled by thermostats. Small fans circulated the air sufficiently that large temperature gradients were

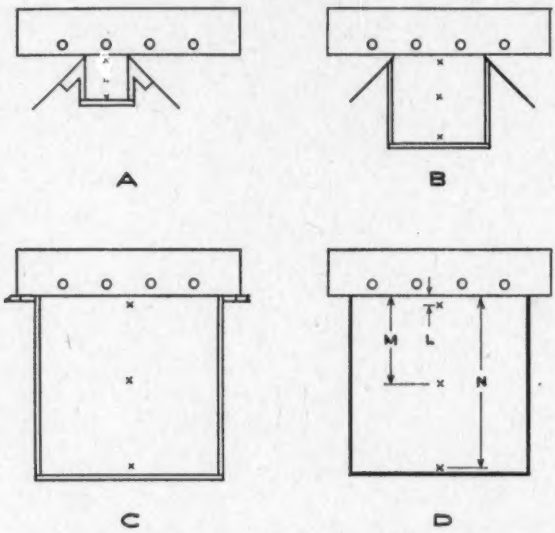

FIG. 4. *Sections of boxes and positions of air thermocouples. X–thermocouple junction.*

eliminated. In general the top chamber was maintained at a temperature of 68.5° F. The temperature of the bottom chamber was always so adjusted that the average temperature over the inner surface of the heat-meter box was approximately 65° F.

The heat-meter box that was used in the first test was made of corkboard and was 6 by 6 in. in cross-section and 8 in. in depth. The arrangement of this box is shown in Fig. 4*A*. The results with this box were not reproducible and it was discarded for measurements of the heat output. It was reduced to a 6 in. cube and used later in measurements of the temperature gradients in the air.

A larger box (17 in. cube) was then used and with this box consistent results were obtained. It appeared, therefore, that the trouble with the 6 in. box was that it was too small and that a sufficient area of the panel

was not covered. Cubical boxes (12 and 24 in.) were also used and these gave results that were consistent with themselves and with the results from the 17 in. box. The conductances of the materials used for making the boxes were measured on a guarded hot-plate apparatus. The description and particulars of the boxes are summarized in Table I.

TABLE I

DESCRIPTION OF BOXES

Box section (Fig. 4)	Inside dimensions of box, in.	Box material	Box conductance B.T.U./hr./sq./°F. diff.	No. of thermocouples		Position of air thermocouples, in. (see Fig. 4*D*)		
				On box	On plaster	*L*	*M*	*N*
A	6 by 6 by 6	½ in. Corkboard	0.50	20	10	5/16	3	5 1/2
B	12 by 12 by 12	½ in. Fiberboard	0.78	32	14	1 1/4	6	11 1/8
B	17 by 17 by 17	½ in. Fiberboard	0.78	32	26	1 1/2	8 7/8	16 3/16
C	24 by 24 by 24	½ in. Fiberboard	0.725	38	20	1 7/8	12 1/16	21 7/8

All temperatures were measured with No. 30 gauge copper-constantan thermocouples. The number of pairs of thermocouples on the boxes varied from 10 to 19. Each couple on the inside surface was opposed by a couple on the outside, and from the differential reading of these opposed couples the temperature difference across the wall was obtained. Since the conductance of the wall was known, it was possible from the temperature difference to calculate the heat that escaped from the box.

The number of thermocouples used on each box is given in Table I and their arrangement on the surfaces of the box is shown in Fig. 5. Table I

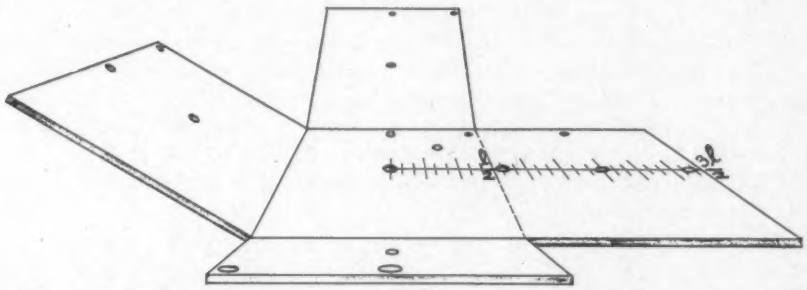

FIG. 5. *View of thermocouples on inside of boxes. 0 — thermocouple junction. (Each thermocouple shown is opposed by one on outside surface.)*

also gives the number of thermocouples used for measuring the surface temperature of the plaster on the panel. The thermocouples on the plaster were inserted into shallow grooves and cemented with glyptal; those on the surfaces of the box were cemented to the surface with glyptal. To determine the temperature gradient of the air within the boxes, three thermocouples were placed in the air directly below the center of the test area at depths indicated in Fig. 4*D* and tabulated in Table I. Later, in order to find whether convection currents were present, it was necessary to measure the temperature of the air at more points within the boxes. For this purpose, 15 thermocouples were placed in the 12 in. and 24 in. boxes at the same heights as those given in Table I. Five thermocouples were arranged at each level in a pattern like the five on a pair of dice. The corner thermocouples were approximately 1 in. from each side wall for the 12 in. box and 2½ in. for the 24 in. box.

Method of Measurement

When measurements were to be taken, the panel was placed in the constant temperature chamber as shown in Fig. 1. The top chamber was then held at a temperature of 68.5° F. By adjusting the flow and temperature of the water in the pipes the heat input to the panel was carefully regulated to bring the surface of the plaster to the desired temperature. At the same time the bottom chamber was cooled sufficiently to bring the average temperature over the inner surfaces of the box as closely as possible to 65° F. When these adjustments were made, the conditions were maintained constant for a sufficiently long time to be certain that equilibrium was established. The temperature of the water in the pipes was then measured and the temperatures of the thermocouples recorded.

Knowing the temperature difference across the walls of the box and the thermal conductance of the material from which it is made, we can easily calculate the amount of heat escaping from the box to the bottom chamber. This must be equal to the total amount of heat that is transferred from the surface of the panel to the box, since under equilibrium conditions there can be no accumulation of heat within the box. It is obvious from the geometry of the arrangement that the temperature of the inside surface and the temperature difference across the walls will not be the same throughout the box and that some system of averaging has to be used. The system adopted was as follows. The temperatures of the box surfaces were plotted on a graph whose abscissas were distances measured along the median line of the box as shown in Fig. 5. Examples of such graphs are reproduced in Fig. 6. From these graphs, eight sections were marked off along the abscissa such that within each section the relation between temperature and distance was approximately linear. The average temperature for each section was then determined. This was done for the temperatures of both the inner and outer surfaces of the box. In this way it is possible from curves such as those shown in Fig. 6 to obtain a mean temperature of the inner surface

which can be used for calculating the average surface temperature (AST) of the box, and a mean temperature difference across the walls for calculating the total heat transfer.

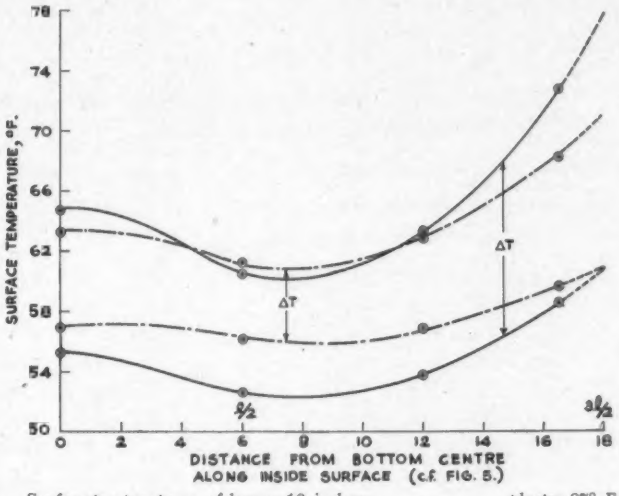

FIG. 6A. *Surface temperatures of boxes: 12 in box: —·—·—·— plaster 87° F.; ——— plaster 104° F.*

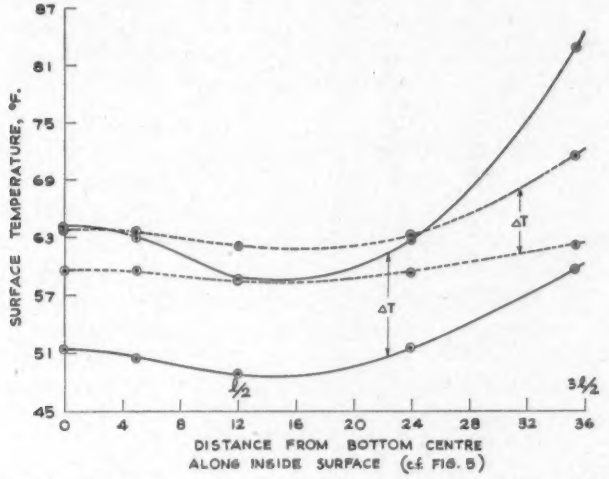

FIG. 6B. *Surface temperatures of boxes: 24 in. box: ---------- plaster 82° F.; ——— plaster 111° F.*

The total heat transferred was calculated from the equation

$$Q_T = C \sum_{i=1}^{i=n} A_i \, (\Delta T)_i, \qquad (1)$$

where Q_T is the total heat which flows through the walls of the box and which is equal to the total heat output downwards for the entire section of the panel enclosed by the box,

C is the conductance of the material of which the box was made,

A_i is the area of the section used for averaging,

$\triangle T_i$ is the average temperature difference between inside and outside surface of box over the section i,

n = number of sections taken for averaging.

To obtain the output of heat per unit area of the panel it is necessary to divide Q_T by the area of panel enclosed by the box.

The curves in Fig. 6 show that the temperatures of the surfaces of the box increase very rapidly as the edge which touches the panel is approached. As shown in Fig. 4 this edge was beveled and the contact with the panel was very narrow. It is improbable, therefore, that the edge took up the temperature of the panel but, on the contrary, it is likely that most of the temperature drop between panel and box took place across the interface. For this reason the curves in Fig. 6 have been extrapolated as shown rather than drawn to meet the panel temperature at the edge.

In computing the area of the walls of the box the inner dimensions were used. It is obvious that the true area for heat transfer would be greater than this, and it might perhaps have been better to have used the mean between inner and outer areas. The total heat calculated from the heat transfer through the walls will, therefore, be slightly low on account of this error.

C. Results and Conclusions

Results

The total heat given off per square foot of the panel to the box is plotted in Fig. 7 for different plaster temperatures. It is to be seen from this graph that the results from the 12 in., 17 in., and 24 in. box are in substantial agreement, and the combined results give a linear relation between heat output and plaster temperature over the range of the measurements. For comparison, the heat output for a full scale installation as calculated by Carrol (3) is plotted on the same graph. In this calculation the air temperature and average surface temperature of the surroundings were taken as 65° F. The emissivity factor F_e was taken as 0.9.

The two curves show immediately that the total output of heat per unit area is not the same for the small panel as for the large installation. The difference must be caused by the contribution of convection to the total heat. As mentioned above, convection will be present in any room and an appreciable amount of heat will be extracted from the panel by this mechanism. On the other hand, in the small boxes used in the laboratory experiment

there are no extraneous sources of temperature gradients, and any transfer of heat by convection will be very small indeed. Carrol's figures do include an estimate for the amount of heat that will be transferred by convection in any full-scale installation. It is possible, therefore, to give from his work the heat output per unit area by radiation alone.

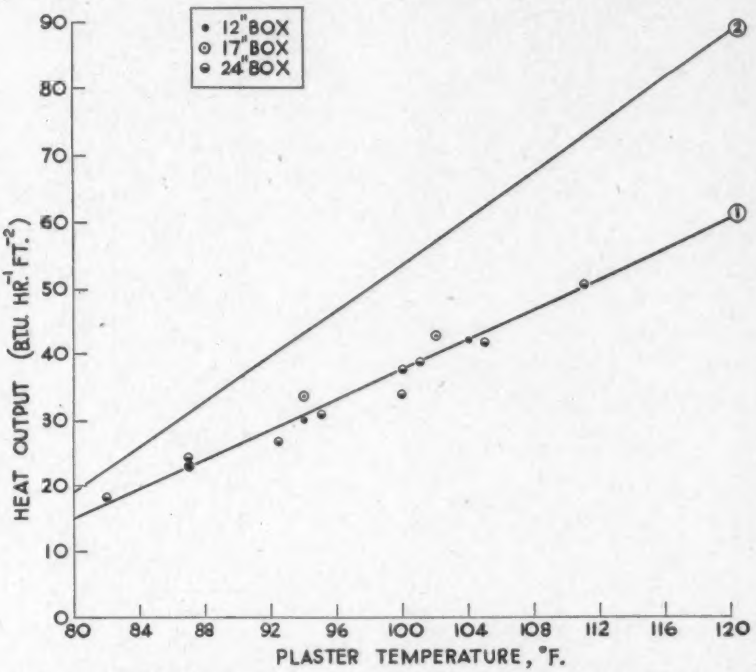

FIG. 7. *Measured heat output. (1) Total heat output in present experiment for MRT = 65° F., $F_e = 0.9$. (2) Total heat output according to Carrol for MRT = 65° F., Air temp. = 65° F., $F_e = 0.9$.*

This has been plotted in Fig. 8 along with the results for the total heat output from the small panels. It is evident that the transfer by radiation alone from the large installation is equal to the total transfer from the small panel. This is strong evidence that all the heat output from the small panel is by radiation and that the effect of convection is, in fact, negligible.

In order to determine whether there was any motion in the air in the boxes the temperature of the air at different positions was measured with thermocouples. Any convection currents would be immediately evident from the distribution of temperature in the box. The distribution of the temperature in a vertical direction along the central line as shown in Fig. 4*D* is reproduced in Fig. 9. In a horizontal plane, it was found that all five thermocouples at one level registered temperatures that were closely the same.

There was, therefore, no indication from air temperature measurements that heat was being transferred by convection. The readings of these air temperature thermocouples were steady and there was no sign of the fluctuations which occur when a small thermocouple is exposed to random air movements in a room. The air in the box could not have been in motion, and all the

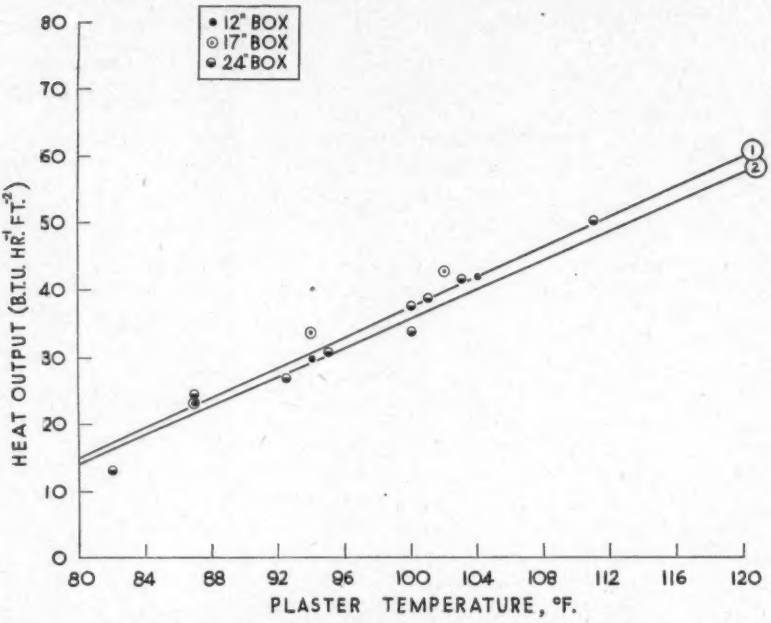

FIG. 8. *Measured heat output compared with radiation heat output for full size panel. (1) Total heat output in present experiments for MRT = 65° F., F_e = 0.9. (2) Radiation heat output for full size panel according to Carrol for MRT = 65° F., F_e = 0.9.*

evidence, therefore, supports the conclusion that the heat transfer by convection was negligibly small and that the measured heat transfer was by radiation alone. In Appendix 1 (below) the measured heat outputs are compared with those calculated from the radiation theory and are shown to agree with the latter.

Conclusions

It is apparent from this experiment that a heat-meter box can be used to measure the radiative heat output from a panel by the method described above. The heat output measured is confined to the heat transferred by radiation, since convection is not present but the whole problem of convective heat transfer from a radiant heating panel is so dependent on extraneous factors that to eliminate it is an advantage. One can limit oneself to radiative heat transfer and, although it will be necessary for the full scale application

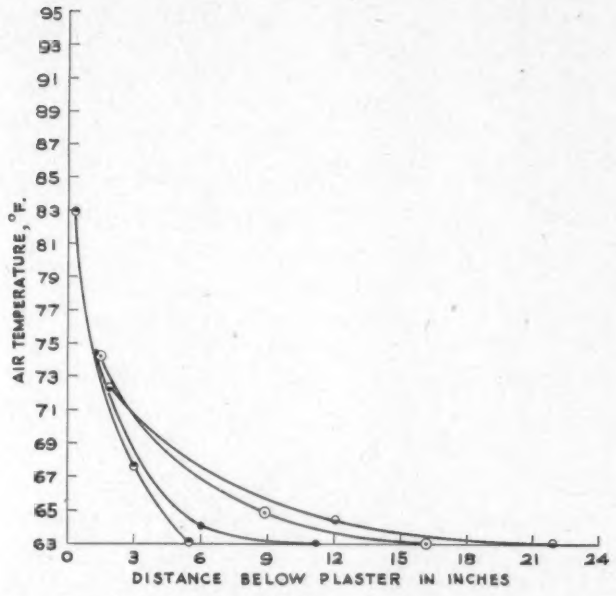

FIG. 9A. *Air temperature within boxes. Plaster, 87° F.*
◓ *6 in. box,* ● *12 in. box,* ⊙ *17 in. box,* ◒ *24 in. box.*

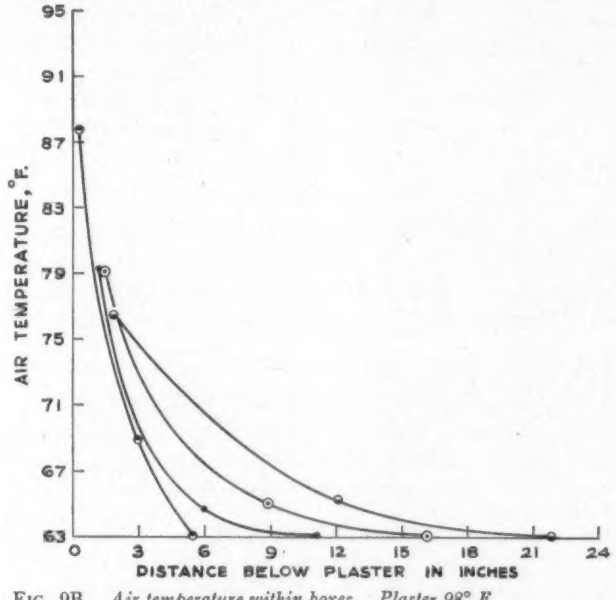

FIG. 9B. *Air temperature within boxes. Plaster 98° F.*
◓ *6 in. box,* ● *12 in. box,* ⊙ *17 in. box,* ◒ *24 in. box.*

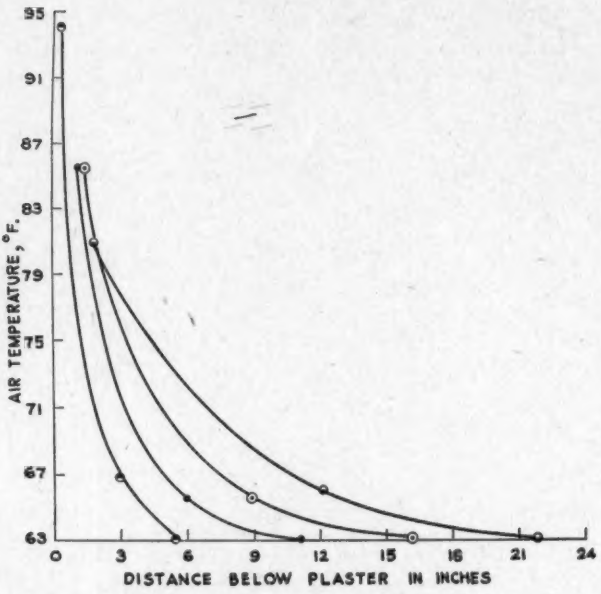

FIG. 9C. *Air temperature within boxes. Plaster, 109° F.*
◓ *6 in. box,* ● *12 in. box,* ⊙ *17 in. box,* ◒ *24 in. box.*

to estimate the additional convective heat transfer, such an estimate will be no worse than that ordinarily applied. It is impossible to make an accurate estimate of convective heat transfer for any radiant heating installation since in no two rooms is convection the same and the laws of convection are not sufficiently precise to allow accurate predictions from design data.

With a laboratory installation such as that described, it would be possible to test relatively cheaply any design of heating panel which might be used. The design factors of pipe size, pipe distribution, depth of plaster, conductance of materials above and below pipes, and the temperature and rate of flow of water could all be varied readily and at small expense and a study of how these factors influence the performance of radiant heating panels could be made.

D. APPENDICES

1. Theory of Radiation and Applications to the Experiment

The fundamental laws of heat transfer by radiation are well known (3, 5, 6, 7), but the calculations even for simple applications prove to be very difficult. At present only the following equation will be considered:

$$Q_R = \sigma F_A F_e A\ (T_1^4 - T_2^4), \qquad (2)$$

where

Q_R = Net heat transferred by radiation from surface 1 to surface 2, B.t.u./hr.

σ = Stefan–Boltzmann constant,
= 0.172×10^{-8} B.t.u./hr., sq. ft., (deg. F. + 460)^4,
F_A = shape factor, dimensionless,
= 1 for completely enclosed surfaces,
F_e = emissivity factor, dimensionless,
A = area of surface 1, sq. ft.,
T_1 = temperature of surface 1, (deg. F. + 460),
T_2 = temperature of surface 2, (deg. F. + 460).

In order to use Equation (2) for the present experiment the plaster surface temperature, T_P, was taken as T_1 and the mean radiant temperature, MRT, of the inner surfaces of the box was taken as T_2. Since the panel surface was completely enclosed by the surfaces of the box, F_A was unity, and since the heat output from 1 sq. ft. of panel area was being considered, Equation (2) could be written as

$$Q_R = \sigma F_e (T_P^4 - MRT^4). \tag{3}$$

Calculation of Mean Radiant Temperature

The MRT was computed from the equation

$$MRT = \sum_{i=1}^{i=13} F_i T_i, \tag{4}$$

where

MRT = mean radiant temperature of the inside surfaces of the box, deg. F.,
F_i = shape factor for area A_i of the box as tabulated below, dimensionless

$$\left(\sum_{i=1}^{i=13} F_i = 1 \right),$$

T_i = average surface temperature of area A_i, deg. F.

Equation (4) is exact for black surfaces, and reasonably accurate for gray surfaces with emissivities in excess of 0.9. Since the emissivity of the box walls was 0.85, Equation (4) should not, strictly speaking, have been used. It was, however, considered sufficiently accurate for the present experiment.

Shape Factors

Hottel has calculated the shape factors for parallel planes (6) and for normal planes with a common edge (5). He has presented the former in graphical form, and Raber and Hutchinson have plotted the latter (7). These graphs were used for calculating the shape factors of the box.

The box was considered as divided into 13 parts, as shown in Fig. 10. The shape factor for A_1, F_1, was taken from Hottel's graph. F_2 was then found by taking F_{1+2} from the graph and subtracting F_1. F_3 was found by subtracting F_{1+2} from 0.2.

The shape factor for A_4, F_4 was found by taking the shape factor of a square relative to an adjacent rectangle (with a common edge) with the shorter side equal to 9/10 of the side of the square from Raber and Hutchinson's graph, subtracting this result from 0.2, and multiplying by 4. F_5 to F_{13} were found by a similar process.

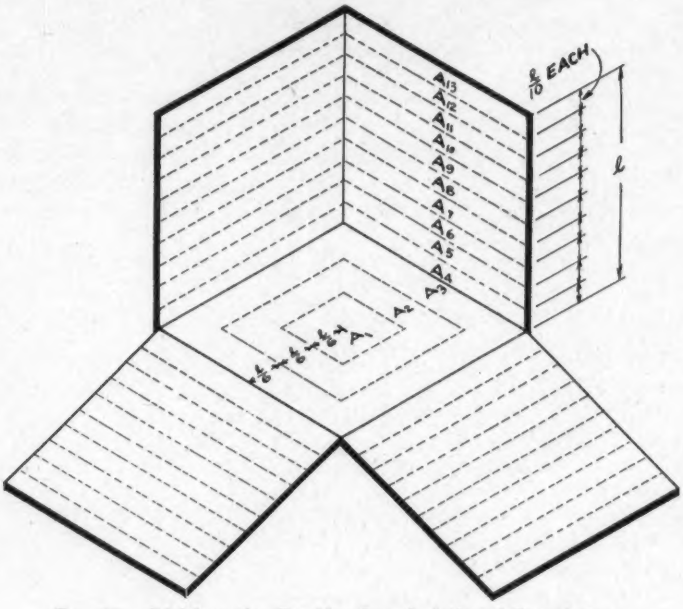

FIG. 10. *Divisions of walls of box for calculation of shape factors.*

The calculations and shape factors thus found are given in Table II.

Emissivity Factor

The emissivity factor F_e of Equation (2) should lie between the limits expressed by the relation

$$e_1 > F_e > \frac{1}{\frac{1}{e_1} + \frac{1}{e_2} - 1}$$

or, for use in Equation (3)

$$e_P > F_e > \frac{1}{\frac{1}{e_P} + \frac{1}{e_W} - 1}, \tag{5}$$

where

e_P = emissivity of the plaster (with respect to a black body),

e_W = emissivity of the inner surfaces of the box (with respect to a black body).

TABLE II

SHAPE FACTORS FOR WALLS OF CUBE AREAS SHOWN IN FIG. 10

	Area	Shape factor	
Bottom	A_1		0.0220
	A_2	0.13 − 0.022	= 0.1080
	A_3	0.20 − 0.13	= 0.0700
Sides	A_4	4 (0.2 − 0.193)	= 0.0280
	A_5	4 (0.193 − 0.1855)	= 0.0300
	A_6	4 (0.1855 − 0.1745)	= 0.0440
	A_7	4 (0.1745 − 0.161)	= 0.0540
	A_8	4 (0.161 − 0.146)	= 0.0600
	A_9	4 (0.146 − 0.1285)	= 0.0700
	A_{10}	4 (0.1285 − 0.1055)	= 0.0920
	A_{11}	4 (0.1055 − 0.07565)	= 0.1194
	A_{12}	4 (0.07565 − 0.04132)	= 0.1373
	A_{13}	4 (0.04132)	= 0.1653
			1.0000

In general, F_A and F_e are not necessarily independent. An exact calculation of a combined factor F_{Ae} can be made for a given situation but this was not carried out for the present work. The emissivities e_P and e_W were measured (Appendix 2) and the limits established by Relation (5) were 0.97 and 0.83.

Method of Plotting Results

When testing, it was difficult to make the AST over the inner walls of the box exactly 65° F., and since the MRT was not equal to the AST, it was necessary to apply a correction to give a result corresponding to an MRT of 65° F. The correction was made as follows. The equations

$$Q_{MRT=65} = \sigma F_e A\,(T_P^4 - (65 + 460)^4)$$
$$Q_T = \sigma F_e A\,(T_P^4 - (MRT + 460)^4)$$

were divided and multiplied by Q_T to give

$$Q_{MRT=65} = \frac{(T_P^4 - (65 + 460)^4)}{(T_P^4 - (MRT + 460)^4)}\ Q_T\ , \qquad (6)$$

where

$Q_{MRT=65}$ = Measured heat output corrected to correspond to an MRT of 65° F., B.t.u./hr., sq. ft. of panel area,
Q_T = Measured heat output as calculated from Equation (1), B.t.u./hr., sq. ft. of panel area,
T_P = Temperature of panel surface, deg. F.,
MRT = Mean radiant temperature of inner surfaces of heat-meter box, calculated from Equation (4), deg. F.

The results of the experiment, as corrected by means of Equation (6), are given in Table III.

TABLE III

RESULTS OF HEAT OUTPUT MEASUREMENTS

Size of box (l in Fig. 10), in.	Plaster temperature ° F	$\overline{AST}$ ° F.	Heat output* Q_T B.t.u./hr., sq. ft. panel area	MRT†, ° F.	$Q_{MRT = 65}$†† B.t.u./hr., sq. ft. of panel area
12	87	63.7	24.6	63.4	23.1
	94	63.4	29.7	65.2	29.8
	104	64.8	39.8	67.2	41.9
17	87	66.4	20.6	67.4	23.0
	94	65.4	31.4	67.1	33.7
	102	66.5	38.9	68.5	42.6
24	82	65.6	17.3	65.8	18.1
	87	67.6	20.5	68.6	24.2
	90.5	65.0	25.1	66.9	26.9
	95	70.2	25.5	70.6	30.9
	100	64.6	33.6	67.2	33.8
	100	65.2	34.8	67.6	37.4
	101	65.4	35.8	67.9	38.6
	105	73.7	31.8	75.2	41.6
	111	65.1	46.7	68.6	50.2

*Calculated from Equation (1).
†Calculated from Equation (4).
††Calculated from Equation (6).

Comparison of Measured Heat Outputs with Theoretical Heat Output

The theoretical heat output by radiation was calculated by means of Equation (3), with F_e equal to 0.97 and 0.83 respectively, and MRT equal to 65° F. The results are shown plotted on a graph in Fig. 11, on which are also plotted the results of the experiment. The full line marked (1) has been calculated with $F_e = 0.97$ whereas in calculating the broken line F_e was taken as 0.83. The measured heat outputs will be seen to compare favorably with the theoretical heat outputs by radiation.

2. Indirect Method of Determination of Emissivities

A guarded hot-plate apparatus, which has been described elsewhere, was used for these determinations. Four samples each 18 in. square were prepared, two for each material to be tested. Each sample had a "sandwich" section, with 1 in. of air between the two surfaces of the material. The test area was 12 in. square, in the central part of the samples, and five thermocouples arranged in the pattern of the five on a die were placed on each of the four surfaces of the material. The thermocouples were placed on the materials, using the same techniques as for placing them on the box and plaster.

The samples were placed in the apparatus and the quantity of heat flowing through the samples was measured, with a convenient temperature difference between the surfaces being tested. Aluminum foil was then placed over the

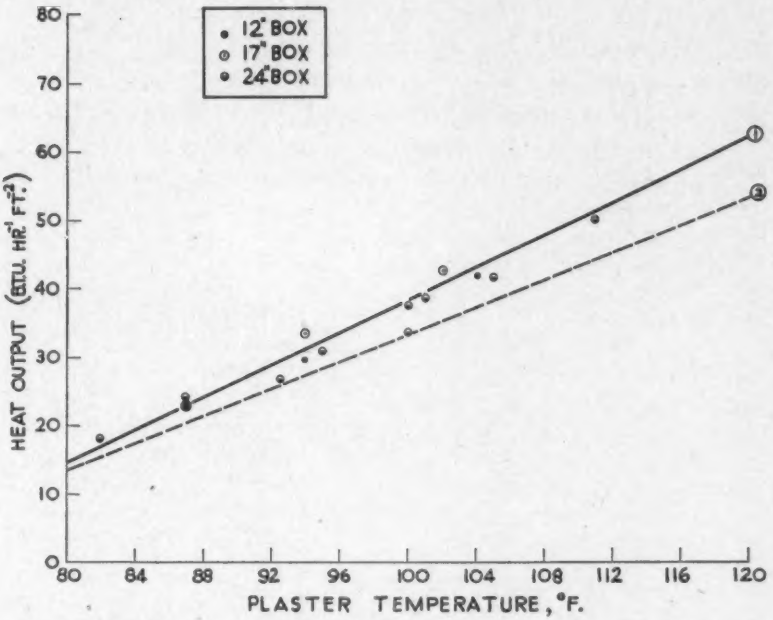

FIG. 11. *Theoretical heat output by radiation calculated from Equation (3). (1) $F_e = 0.97$, MRT = 65° F. (2) $F_e = 0.83$, MRT = 65° F.*

surfaces and the quantity of heat flowing was measured with several temperature differences close to the first. These were plotted on a graph so that the quantity of heat which would flow with the first temperature difference could be read from the graph. The emissivity of the material was then calculated, using the following equations:

$$Q_1 = C'\triangle T_1 + \sigma F_{e1}(T_1^4 - T_2^4), \tag{7}$$

$$Q_2 = C'\triangle T_1 + \sigma F_{e2}(T_3^4 - T_4^4), \tag{8}$$

$$Q_2 = C''\triangle T, \tag{9}$$

$$F_e = \frac{1}{\frac{2}{e} - 1}, \tag{10}$$

where

Q_1 = Quantity of heat flowing through sample without aluminum foil, B.t.u./hr., sq. ft.,

C' = Coefficient of convection and conduction, B.t.u./ hr., sq. ft., °F.,

$\triangle T_1 = T_1 - T_2$ = Temperature difference between surfaces of samples without aluminum foil, ° F.,

$\sigma = 0.172 \times 10^{-8}$ B.t.u./hr., sq. ft., (°F. + 460)^4,

T_1, T_2 = Temperatures of samples without foil, (°F. + 460),

T_3, T_4 = Temperatures of foil-covered samples, (°F. + 460),

F_e = emissivity factor for infinite parallel planes, defined by Equation (10) for identical surfaces,

Q_2 = quantity of heat flowing through foil-covered samples, B.t.u./hr., sq. ft.,

C'' = secondary coefficient of convection and conduction as determined by hot-plate apparatus, B.t.u./hr., sq. ft., °F.,

e = emissivity of surfaces of materials, with respect to a black body.

Q_1 and ΔT_1, T_1 and T_2 were first measured with no aluminum foil. Several values of Q_2 and C'' were then measured with foil-covered samples and C'' for ΔT_1 read from a graph of C'' against ΔT. Q_2 for ΔT_1 was then determined from Equation (9). The emissivity of the aluminum foil was assumed to be 0.05. F_{e2} was calculated from Equation (10) using this value. $C'\Delta T_1$ was now calculated from Equation (8) and substituted into Equation (7), from which F_{e1} was calculated. The required emissivity was now calculated from Equation (10).

The results are given in Table IV.

TABLE IV

RESULTS OF TESTS FOR EMISSIVITIES

Material	Condition	Q_1 B.t.u./hr. ft.^{2}	ΔT °F.	$\frac{T_1+T_2}{2}$ °F.	Q_2 B.t.u./hr. ft.^{2}	T_3-T_4 °F.	$\frac{T_3+T_4}{2}$ °F.	C'' B.t.u./hr. ft.^{2} °F.	e
Fiberboard	Bare	19.9	18.5	66.6					
	Covered with aluminum				13.2	32.7	67.7	0.404	
					9.26	24.6	58.8	0.377	
					6.02	17.6	65.3	0.342	
	From graph and calculations					18.5	65.6	0.35	0.85
Plaster	Bare	85.0	53.8	103.5					
	Covered with aluminum foil				25.3	56.1	76.4	0.450	
					26.0	56.9	76.8	0.457	
					21.3	48.8	71.0	0.436	
	From graph and calculations					53.8	74.1	0.45	0.97

Acknowledgments

The author wishes to make grateful acknowledgment to Dr. C. D. Niven, under whose direction these experiments were carried out, and to Mr. R. A. Ross, who assisted during the earlier parts of the work.

Acknowledgment is made also to Dr. J. D. Babbitt, who suggested the indirect method of determining emissivities described in Appendix 2, and who gave valuable criticism during the writing of this paper.

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A MODIFIED BRUCINE METHOD FOR THE DETERMINATION OF NITRATE[1]

APPLICATION TO MEAT AND SOIL

By D. MacDougall[2] and F. E. Roadhouse[3]

Abstract

A modified brucine method for the determination of small amounts of nitrate in biological material is described. Error due to instability of the reagent has been overcome by dissolving the brucine in 91% ethanol. A 10% solution of the alkaloid was found to be most satisfactory and was stable for up to a year. Less color is developed with the ethanol solution than with other commonly used solvents and the effective working range of the method is thus increased approximately five times. Chloride does not interfere seriously but nitrite must be removed (by adding urea and boiling) prior to the determination. Organic matter in the sample may char slightly when the concentrated sulphuric acid is added but this error is compensated for by appropriate blanks. The method has been applied successfully to cured meat and to soils, and excellent recoveries of added nitrate have been obtained. The results agree with those obtained by the gasometric method but are higher than those obtained by the phenoldisulphonic acid procedure.

Introduction

Colorimetric methods for the determination of nitrate based on phenoldisulphonic acid (6, p. 631) or *m*-xylenol (4) are cumbersome, as proteinaceous material and chloride must both be removed. The brucine method, on the other hand, has been used in the presence of chloride (8), organic matter (5), and nitrite (7, p. 635). However, some workers have claimed that the results are inconsistent (2, 9), and further study of the method was therefore undertaken. Details of a modified method are given at the end of this paper.

Development of Method

Preparation of the Brucine Reagent

Preliminary determinations on sodium nitrate solutions by the earlier procedures (3, 10) indicated that part of the difficulty in obtaining consistent results (2, 9) was due to instability of the brucine reagent. Possible solvents for the alkaloid were therefore investigated and ethanol appeared promising.

The effect of increasing amounts of brucine on the color developed was studied by preparing standard curves using 1 ml. of 5, 10, 20, and 40% solutions of brucine in 95% ethanol. All other conditions were maintained constant. Fig. 1 presents the results obtained and indicates that the color density obeyed Beer's law best at the highest brucine level. However,

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brucine tended to crystallize from the more concentrated solutions, and replicate determinations indicated that more consistent results were obtained with the 10% solution. Some brucine occasionally crystallized out of the 10% solution, but the addition of enough distilled water to reduce the ethanol concentration to 91% overcame this difficulty. Reagent prepared in this manner was stored at room temperature for 12 months without deterioration as determined by analytical results.

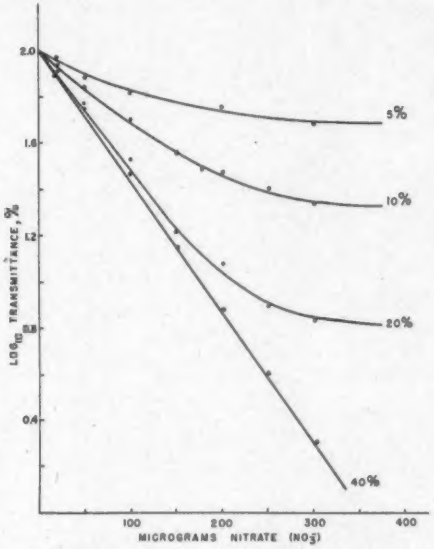

FIG. 1. *Effect of increasing brucine concentration in 95% ethanol.*

Interfering Substances

Additions of reagent grade sodium chloride had no demonstrable effect on the apparent nitrate content of standard solutions. However, the addition of commercial grade sodium chloride to aqueous nitrate solutions changed the shape of the transmission–concentration curve as shown in Fig. 2. Each point in this figure is the mean of four observations. An analysis of variance showed that the difference between salt and no salt was highly significant (1% level). Addition of mild oxidizing or reducing agents did not prevent the effect although it disappeared after the solutions had been standing for a few days. As solutions containing commercial sodium chloride (meat pickling solution, etc.) are usually allowed to stand for some time before nitrate is determined this effect is probably not serious.

Addition of nitrite is claimed (7, p. 635) to have no effect if the final solution contains two parts of sulphuric acid for every part of water, but under the conditions of the present studies some color was produced by nitrite even

when the proportion of sulphuric acid to water was as high as 4 to 1. The amount of color produced by nitrite was variable, and it was therefore necessary to destroy the nitrite before proceeding with the nitrate determination. A modification of Acel's procedure using urea (1) was adopted for this

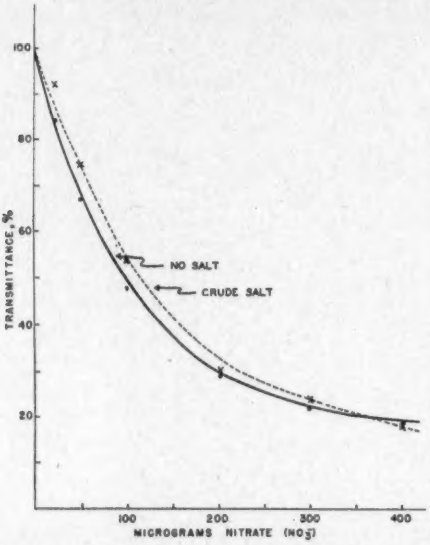

FIG. 2. *The effect of crude sodium chloride on the shape of the calibration curve.*

purpose. The data presented in Table I show that nitrite is completely removed by this method and that no loss of nitrate occurs.

Organic matter chars when concentrated sulphuric acid is added to the aqueous extract, and special provision had to be made to correct for the color formed in this way. This was accomplished by determining the intensity

TABLE I

EFFECT OF NITRITE REMOVAL ON THE APPARENT NITRATE CONTENT OF STANDARD SOLUTIONS

Nitrate added, μgm./ml.	Nitrate found, μgm./ml.	
	Nitrite added*	Nitrite absent
2	2.0	2.0
5	4.8	4.8
10	10.2	10.3
15	14.6	15.2
20	20.0	20.0
25	25.0	25.0
30	29.8	30.0
40	40.0	40.0

**20 μgm. per ml. of nitrite added and then destroyed by boiling with urea.*

of the color and correcting the setting of the water blank accordingly. The validity of the correction was tested on two series of nitrate solutions to which sucrose had been added. The data, presented in Table II, show that excellent results can be obtained even in the presence of relatively high concentrations of organic matter.

TABLE II

EFFECT OF SUCROSE ON THE APPARENT NITRATE CONTENT OF STANDARD SOLUTIONS

Nitrate added, μgm./ml.	Nitrate found, μgm./ml.	
	25 μgm. sucrose/ml.	50 μgm. sucrose/ml.
2.0	2.1	1.9
5.0	5.0	5.0
10.0	10.0	9.6
15.0	14.6	15.0
20.0	20.0	19.7
25.0	24.5	25.0
30.0	29.5	30.0

Effect of Variations in Procedure

Varying the time between the addition of brucine reagent and sulphuric acid, or between addition of acid and placing the flask in the cooling bath, from 0 to 20 min. had no demonstrable effect on the final color. Nevertheless, it is recognized that the procedure is empirical. To obtain accurate results close attention to detail and rigid control of all possible variables are required.

Precision of Method

The method has been applied to the determination of nitrate in meat extracts prepared by hot water extraction (9) and in soil extracts prepared by calcium oxide extraction (6, p. 18). The data obtained with meat (Tables III and IV) show good agreement between the results by the gasometric (6, pp. 423–424) and the present method, but the phenoldisulphonic acid procedure (9) appears to give low results. The phenoldisulphonic acid method included precipitation of chloride with silver sulphate and protein with

TABLE III

COMPARISON OF RESULTS OBTAINED BY THREE METHODS ON VARIOUS MEATS

Material	Sodium nitrate, %		
	Gasometric method	Phenoldisulphonic acid method	Brucine method
Military bacon	0.327	0.179	0.352
Sugar cured ham	0.093	0.060	0.088
Shoulder butts	0.220	0.140	0.237
Export back	0.160	0.051	0.150

TABLE IV

RECOVERY BY THE BRUCINE METHOD OF NITRATE ADDED TO MILITARY BACON

Nitrate added, %	Nitrate found, %	Recovery of added nitrate, %
0.000	0.345	
0.150	0.495	100
0.300	0.645	100
0.450	0.810	103

lead acetate. Loss of nitrate may have occurred at this stage. Good recoveries of added nitrate were obtained with the modified brucine procedure. Table V presents the data from the soil analyses; higher results and better recoveries were again obtained with the brucine than with the phenoldisulphonic acid method.

These results indicate that the proposed method is equal in accuracy to the gasometric method and is preferable to the phenoldisulphonic acid method. Within the range of 5 to 25 μgm. of sodium nitrate per milliliter of sample the error of estimation appears to be about 5%.

TABLE V

COMPARISON OF THE BRUCINE AND PHENOLDISULPHONIC ACID METHODS ON VARIOUS SOILS

Soil type	Nitrate content of original soil, p.p.m.		Nitrate content after adding 100 p.p.m.		Recovery of added nitrate, %	
	Brucine	Phenoldisulphonic acid	Brucine	Phenoldisulphonic acid	Brucine	Phenoldisulphonic acid
Clay	85	68	187	166	102	98
"	77	74	176	172	99	98
"	24	17	119	108	95	91
Clay loam	39	25	143	121	104	96
" "	74	61	180	163	106	102
" "	13	10	112	90	99	80
Sandy loam	83	80	182	174	99	92
" "	76	84	177	192	101	108
Sand	4	3	101	88	97	85

Recommended Method

Reagents

Brucine reagent—dissolve 10 gm. of brucine alkaloid (Merck and Co.) in approximately 80 ml. of 95% ethanol, add 3 ml. of distilled water, and make to a volume of 100 ml. with 95% ethanol. The reagent is stable for several months.

Sulphuric acid, reagent grade, concentrated—if traces of nitrate are present in this reagent they must be removed by shaking with mercury (7, p. 633).

Sulphuric acid (1 *N*)—28 ml. of concentrated sulphuric acid diluted to 1 liter with distilled water.

Urea, 10% solution—dissolve 10 gm. of reagent grade urea in distilled water and make to 100 ml. volume.

Procedure

Place a 10 ml. aliquot, containing 50 to 250 μgm. of sodium nitrate, of the solution to be analyzed in a 50 ml. volumetric flask. Add two or three drops of 1 *N* sulphuric acid and 1 ml. of urea solution and boil the mixture gently for five minutes. Loss of vapor from the flask must be kept to a minimum during boiling. Cool, add 1 ml. of brucine reagent, followed by 20 ml. of concentrated sulphuric acid. Mix the contents of the flask by vigorous swirling during the addition of both the brucine and the acid. Allow the flask to cool in air for five minutes, and in a cold water bath for 20 min., then add a second 20 ml. of concentrated sulphuric acid, with swirling, and replace the flask in the cold water bath. When cool (about five minutes) adjust the volume to 50 ml. with concentrated sulphuric acid and mix the contents of the flask thoroughly.

Prepare a blank from a second aliquot of the sample by subjecting it to the procedure outlined except that 1 ml. of 91% ethanol is added in place of the brucine reagent. Also prepare a distilled water blank containing all reagents but no nitrate.

Transfer 10 to 15 ml. of the solution to a colorimeter tube and allow a few minutes for the escape of air bubbles. Adjust the instrument (an Evelyn photoelectric colorimeter was used in these studies) to 100 with a tube containing distilled water only and then determine the intensity, at 4200Å, of the color due to charring in the sample blank (no brucine). Place the water blank (no nitrate) in the instrument and adjust the setting to $85 \times \frac{100}{\text{sample blank}}$. For example, if the sample blank gives a reading of 95, the water blank will be set to $85 \times \frac{100}{95} = 89.5$. Eighty-five is, of course, an arbitrary figure sufficiently below 100 to allow this correction to be made.

Read the transmittance of the samples against this setting, and determine the nitrate content by reference to a previously prepared standard curve. Note that the standard curve must be prepared so that zero sodium nitrate corresponds to a setting of 85 on the galvanometer.

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